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REPORTS ON THE PROGRESS OF APPLIED CHEMISTRY

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REPORTS

ON THE

PROGRESS OF APPLIED CHEMISTRY

FUEL

By L. HORTON, Ph.D., B.Sc., A.R.C.S., D.I.C., A.R.I.C.

Fuel Research Station, Department of Scientific and Industrial Research

THE year 1949 saw the passing of the gas industry into national ownership which took effect on May 1. The Minister of Fuel and Power had previously announced[1] the names of the chairmen of the twelve 'Area Boards' set up under the Act which nationalized the industry.

The National Coal Board issued its report and statement of accounts for the year 1948,[2] the second year of public ownership, and announced a surplus on the year's working of £1,651,965 compared with a deficit of £23,255,586 for the previous year. A large number of coals are being analysed and their value assessed, in order to assist the Board to utilize them more effectively, and also to formulate a more suitable system of pricing. The Board hopes consumers will buy more of those coals which are cheapest to produce and deliver, and less of those which make heavy demands on the transport services of the country.

The Minister of Fuel and Power stated[3] that research and development work on the utilization of coal undertaken by various official and public bodies cost about £450,000 per annum. In addition the Ministry spent annually a further £120,000 on research on safety in mines. Bituminous Coal Research Inc., Pittsburgh, Pa., announced[4] for the second year in succession the authorization of the expenditure of $500,000 on research.

The Committee on Industrial Productivity issued its first report.[5] An adequate supply of good coal is considered to be one of the chief basic requirements of industry if increased productivity is to be achieved. It suggests that increased coal production would be realized by the installation of new underground haulage systems and new coal-cleaning plants. The report of the National Coal Board[2] discloses the awareness of the Board to these questions and its efforts to satisfy them.

A prolonged strike by miners in New South Wales led to a serious disruption of the economic life of Australia and to the acute realization of the dependence of the country upon the deep-mined coal for many of its essential services. An inquiry has accordingly been instituted to see whether the brown coal of Victoria can be used for gas-making for domestic and industrial purposes.[6]

Fuel resources and production

As a result of a deep bore made at Whittington Heath, near Lichfield, Staffordshire, coal deposits were found[7] which it is considered will add

at least 80 yr. to the producing life of the district at the present rate of mining. Coal was first encountered at a depth of 3000 ft., and between 3000 and 3400 ft. an aggregate of 30 ft. of coal was found including three seams of 8, 6 and 5 ft. in thickness. The deposits when completely surveyed may well add as much as 2000 million tons to our coal resources.

The South-Western Regional Coal Board announced[8] that a geological survey had indicated that there were prospects of obtaining millions of tons of coal, hitherto thought to be unworkable, from the area lying between Tondu, near Bridgend, and Port Talbot. The steep dip, up to 30°, of the measures in this area creates big practical difficulties in winning the coal but it is thought they may be overcome by modern mining methods. Six workable seams of 5 ft. average thickness have been proved and nine others show considerable promise.

The output of deep-mined coal in this country for the year 1948 was 197,600,000 tons; a further 11,700,000 tons of opencast coal was obtained, bringing the total amount to 209,300,000 tons.[2] A considerable increase in underground mechanization took place during this period. The "Statistical Digest" for the years 1946 and 1947[9] published by the Ministry of Fuel and Power contains details of coal production for the period and states that 75% of the coal produced was cut by machine in 1947.

The desirability of a survey of the coal resources of the British Commonwealth has been stressed by Carlow.[10] The total resources are estimated to be 329,393 millions tons; the current annual production is 300,300,000 tons.

The coal resources of South Australia have been reviewed by Dickinson.[11] The Leigh Creek coalfield, about 380 miles from Adelaide and 170 miles from Port Augusta, has an estimated content of about 380 million tons but only about 30 million tons will be available to open cut working. Brown coal deposits amounting to 225 million tons have been shown to be present within 80 miles of Adelaide, but only at one place, Moorlands, will they be reached by open cut working. At this place they are expected to yield about 20 million tons. The exploration of the Leigh Creek and Moorlands fields has been described by Parkin.[12] Three coals, two from the Leigh Creek and one from the Moorlands area, have been examined by Parker.[13] He concluded that all three would be unsuitable for burning on mechanical stokers but that the two Leigh Creek coals would be satisfactory for pulverized fuel firing. None would give a satisfactory coke on carbonization and the gas would not be suitable for distribution as town's gas.

The large-scale development of the Blair Atholl coal-field has been considered.[14] The field has estimated reserves of not less than 200 million tons of non-coking coal, low in ash, with an average calorific value of 11,600 B.Th.U./lb.

High-grade coal occurring in seams varying in thickness from 10–70 ft. has been discovered in the Springs–Witbank area of South Africa.[15] The nearness of the coal to the surface will make it amenable to open cast working. A new field of coking coal about 37 square miles in extent has been discovered in Southern Rhodesia, about 150 miles from Bulawayo.[16]

The coal resources of Tanganyika[17] and Nyasaland[18] have been reviewed. The resources of other parts of the Commonwealth have been considered, e.g. New Zealand,[19–21] Canada,[22,23] and India.[24]

The coal reserves of the U.S.A. amount to about 3·1 million million tons or about 40% of the total world's reserves.[25] Production in 1947 of soft coal was 630,623,622 tons; 61% of the total underground output was loaded by machinery.[26] Production in 1948 fell to 594 million tons.

The discovery was announced of a new coal field in the Huainan basin of Central China;[27] 27 seams with an aggregate thickness of 128 ft. of coal have been found, two of which are suitable for making high grade metallurgical coke. All the seams lie within 2000 ft. of the surface. The exploitation of coal deposits in other parts of the world, e.g. Upper Silesia,[28] Japan,[29] Belgian Congo,[30] Chile,[31] Brazil,[32,33] has been described.

Peat.—A sum of £50,000 is to be made available from Development Fund grants for experiments into the exploitation of the Scottish peat deposits.[34]

Physical and chemical properties of coal

Flora and fauna of coal.—Thiergart[35] has described the pollen grains of the shrubs of the middle tertiary period. Petrascheck[36] has made a study of artificial coalification using an autoclave and subjecting wood and coals of various ranks to the action of elevated temperature and pressure. He showed that cellulose rapidly decomposed and concluded that vitrain was formed from lignified tissue and durain from moor peat.

Physical properties of coal

The important researches carried out by the British Coal Utilisation Research Association on the physical properties of coal have been continued and further publications have appeared. Bond, Griffith and Maggs[37] have discussed the relation between water in bulk and that adsorbed on coal. It might be expected that capillary condensed water would possess the properties of water in bulk but there was no evidence of a sharp freezing point when coal saturated with water vapour was cooled. The authors concluded that a difference in phase exists between water in bulk and that adsorbed on coal.

The heat of wetting of finely ground coal with methanol has been used[38] to determine to what extent fresh surface is produced when coal is ground to various degrees of fineness. It was found that if the size of the coal was progressively reduced to the size which just passed through a 240 B.S. test sieve, no appreciable fresh surface was produced but the internal surface was made progressively more accessible to the wetting liquid as the size reduction proceeded. More drastic grinding, however, considerably increased the sorptive power of the coal for the alcohol. The effect was considered to be due to the formation of fresh internal as well as external surface. There appears to be a limit to the increase in total surface of any coal which may be brought about by fine grinding.

Franklin[39] has continued her studies of true and apparent densities of coal. Coals ground to pass a 72 B.S. test sieve were found to have their pore space rapidly and completely filled by gaseous helium, which

therefore permits a determination of the true density to be made. Determinations of density using different liquids, however, gave widely varying results. This was due not only to the different changes in volume experienced by the coal when in contact with the various media but also to the fact that the total pore space was, in general, no longer completely accessible to the different liquids. The degree of accessibility varied from liquid to liquid. It was concluded that the pores of coals contained numerous fine constrictions, whose width was of the diameter of simple molecules but varied with the rank of the coal. The investigations have also shown that a linear relation exists between the specific volume of coals and their hydrogen contents. Since the extrapolated value of the specific volume of a hypothetical coal of zero hydrogen content is very different from the value for graphite, it was concluded that the structures of coal and graphite are markedly different and that graphite cannot represent the final stage in the coalification process.

Brusset[40] has studied the colloidal structure of coals by X-ray diffraction and has concluded that coal is formed of micelles, 40–200 A. in diameter, which are composed of humic matter and arranged in approximate graphitic structure surrounded by carbonaceous material with a different electronic density.

Chemical properties of coal

Inorganic constituents.—Reynolds[41] has reported the presence of a number of unusual elements, V, Cr, Ti, Ni, in the ashes from vitrains from North Wales and North Staffordshire. The germanium content of some Transcarpathian coals was found[42] to be greater in the outer layers than in the main body of the coal—a result which may be due to adsorption by the coal from aqueous solution. Other workers[43] have found no connexion between the germanium content and the location of the seam. Mason[44] has pointed out that the solution, transportation and deposition of many elements depend on the oxidation potential of the environment and that strongly reducing conditions, such as exist in marine muds, favour the enrichment of these decaying organic deposits by such elements as Ge, Ga, Mo, Ni, and Co.

Oxidation of coal.—The exposure of freshly ground undried coal to the atmosphere has been shown by Jones and Townend[45] to result in the formation of peroxidic bodies on the coal surface provided the exposure is made at a temperature below 70° c. Under these conditions little oxygen enters into combination with the main coal substance; carbon monoxide is the main gaseous product. When a peroxidized coal was heated above 70° c. its peroxide content was found rapidly to disappear and carbon dioxide formed the principal gaseous product. When the oxidation was effected above 70° c. little peroxide formation occurred but considerable amounts of oxygen entered into combinatin with the coal substance and brought about a marked increase in its solubility in sodium hydroxide. The presence of moisture was shown to be essential for the formation of the peroxidic bodies. Carbon also was found to give rise to peroxides under similar conditions of oxidation. Thus 70° c. is the critical temperature for the stability of the coal- or carbon-water-oxygen complex and marks the onset of a different oxidation reaction

of the coal substance. Similar peroxidic bodies have been found[46] in the carbonaceous deposits which are found in compressed air systems in which explosions have occurred, and it has been suggested that they may have played a significant part in the initiation of the explosion.

A study of the controlled oxidation of coal at temperatures up to 325°c. has been made by Friedman and Kinney.[47] A process for the making of organic acids from carbonaceous materials by oxidation has been patented by Kiebler.[48]

The electrolytic oxidation of vitrain by Belcher[49] using a copper anode produced both ulmins and water-soluble acids. Since, however, ulmins proved to be incapable of further degradation under these conditions of oxidation it was concluded that vitrain must oxidize in two distinct ways.

Humic acids.—A study has been made by Ahmed and Kinney[50] of the thermal decomposition of humic acids prepared from bituminous coal by treatment with nitric acid. Carbon dioxide (20%) and water (14%) formed the principal volatile products. Carbon monoxide amounted to only 2·1%. On the assumption that the carbon dioxide arose exclusively from carboxyl groups and the water from hydroxyl groups, each equivalent weight of humic acids, approximately 322, contains two hydroxyl groups to one carboxyl. Polansky and Kinney[51] found that the determined molecular weights of humic acids prepared in the same way were higher in acetamide (342) than in catechol (201). The actual values were found to be affected by the nature of the solvent used for the extraction of the ulmins from the acid-treated coal. Differences in the solubility of humic acids in acetone have been shown[52] to be due to slight differences in hydration.

Hydrogenation studies.—It has been shown by Storch[53] and his colleagues that the use of a vehicle such as tetralin which can act as a hydrogen carrier does not necessarily ensure good liquefaction. In fact hydrogen gas appears to be a more effective hydrogenating agent than transferred hydrogen. Glenn[54] has described the small-scale hydrogenation of selected American bituminous coals at temperatures from 325 to 400° c. using calcium copper chromite catalyst. Japanese workers have described[55] the hydrogenation of a number of different coals of varying rank with and without catalyst and vehicle. The absence of the vehicle was always unfavourable and especially so with high-rank coals.

Solvent extraction.—Dryden has shown[56] that certain basic solvents are capable of dissolving or dispersing such large proportions of the low rank bituminous coals at atmospheric temperature that they may be regarded as specific solvents for this type of coal. The main types of specific solvents are aliphatic compounds containing at least one primary amino group, aromatic compounds containing at least one primary amino group attached to an aliphatic side chain and certain heterocyclic compounds. One such specific solvent is ethylenediamine whose solvent effect on a number of coals has been studied. The yield of extract diminished as the rank of the coal increased above a carbon content of about 80%. The same author has reviewed the whole subject[57] of solvent extraction of bituminous coals. The influence of

various types of solvent on the solubility of bog head coals has been examined by D'Yakova and Davtyan.[58] An account by Frese of the laboratory and large-scale operation of the Pott–Broche process has appeared.[59]

Hydrolysis.—Berkowitz[60] has suggested that the fact that certain coals are more soluble in boiling alcoholic potassium hydroxide than in aqueous caustic potash may be due to the hydrolysis of an ester-like component of part of the coal substance.

Coal mining and preparation

The problems of coal conservation and the general causes of low extraction have been discussed by Boyd[61] and he has described a number of relevant investigations in progress at the U.S. Bureau of Mines. These latter may be grouped as follows: (i) more complete extraction and improved transportation, (ii) more efficient preparation, (iii) safer mining practices.

The problems introduced by more complete extraction are many and varied and depend on the mining conditions which prevail. Increased mechanical stowage has greatly improved roof support.[62] Underground mechanical haulage, both conveyor belt and Diesel locomotive, has increased considerably. The conditions which must be satisfied to ensure the safe usage of Diesel locomotives have been described by East and Maize[63] and Elliott.[64] Alcock[65] has reviewed their use in British pits. A comparison of belt conveyor and locomotive haulage has been made by Winkhaus[66] with reference to the conditions which prevail in Germany, U.S.A. and in this country. The introduction of horizon mining in steeply inclined seams in South Wales has been described[67,68] and should lead to improved production in these conditions. The report of the National Coal Board[2] indicates the extent of the increase in coal-cutting and loading machinery introduced into British pits and of the increased coal cleaning facilities. Preliminary trials of fluorescent lighting in certain pits have been announced.[69,70] The control of gas emission from coal seams by drawing off the gas in advance of the workings by means of bore holes not only ensures safer working conditions but also permits the collection and utilization of a valuable gaseous fuel. At Hirschbach Colliery (Saar) the daily production of gas is 530,000–635,000 cu.ft. (85% methane).[71] The conditions have been described[72,73] which are favourable for the use of the technique. An analysis of the causes of spontaneous underground fires has been made by Jablecki.[74] Over 90% of all fires are associated with bord and pillar workings but the risk is greatly diminished by efficient mechanical stowage. The inclination of the seams and the presence of pyrites play no obvious part in the matter. The question has been reviewed by Schultze-Rhonhof and Klinger.[75]

The risk of pollution of public water supplies arising from open cast workings has been stressed by Snyder[76] and details have been given of a case of serious pollution which occurred at Allegheny, Pa.

Some of the objects have been outlined[77] of the second experiment on underground gasification which is being carried out at Gorgas, Alabama by the U.S. Bureau of Mines and the Alabama Power Co. The work on

this subject which has been carried out in Italy and Russia has been reviewed by Minchin.[78]

Coal dust problems

An account has been given[79] of experiments at the Hilton Main Colliery, Staffs., in which steam is infused into holes in the coal face, 3–4 ft. apart and about half way between roof and floor, in an effort to suppress dust formation. Hay,[80] in reviewing the problem as it occurs in British mines, states that in South Wales 1000 miles of steel water pipes have been installed and 40 miles of coal face are equipped with systems of dust control. The use of water infusion in steep and semi-steep coal formations has been described by Rolshoven and Heitmann.[81] A review of pneumokoniosis and dust suppression in mines has been published by Heppleston.[82] King[83] has surveyed the problem of the origin and treatment of silicosis and has emphasized the need for further study before aluminium therapy can be finally accepted. A comprehensive review has also been published by Janssens and Gandibleux.[84]

Handling and storage of coal

Hurysz[85] has described in detail the precautions which must be adopted to ensure the safe storage, for periods of the order of three years, of large quantities of coal containing considerable fines. These conditions are those that prevail in Poland at the present time. He recommends that the coal dumps shall be in the form of truncated prisms constructed on level bases, 60 × 150 m., with their longer sides parallel to the direction of the prevailing wind. They should not exceed 4 m. in height and preferably should be compacted mechanically. The Fire Protection Association has issued a booklet[86] dealing with the prevention of fires in coal stacks. The Ohio Coal Association has published a bulletin[87] detailing methods of efficient coal storage.

Coal cleaning.—The problem of coal washing has been considered by Teissier[88] from the standpoint of the laws of probability. A useful review of recent progress in coal preparation has been published by Swartzman[89] and deals with heavy media processes, the treatment of fines, the possibility of petrographic separation and the isolation of resins from coal especially those from United States and Canada. Voznyi[90] has studied the distribution of sulphur among the various washery fractions of a high sulphur coal. In general, the larger sizes of any particular gravity fraction were found to contain the greater amounts of sulphur.

Briquetting.—The importance of correct sizing and moisture content of fine coal which is to be compacted into pellets is apparent from the work reported by Day and Wright.[91] Silts of fine coals varying in rank from sub-bituminous to anthracite were successfully extruded without the use of a binder to give pellets with a moisture content of 13–20%. In this condition the pellets were very friable but their strength steadily increased as drying progressed. Similar investigations on a pilot-plant scale using anthracite fines have been reported.[92] Economies in the amounts of pitch required to make satisfactory briquettes have also been effected[93] by suitable sizing of the coal and adjustment of its water content.

Coke properties and production

A study of the heat of coking has been made by Tettweiler[94] for a series of Ruhr coals carbonized at a mean temperature of 1000° c. The value was found to be exothermic and to vary from 200–475 k.cal./kg. depending on the moisture and volatile contents of the coal. For a constant volatile content within the range from 20 to about 31% the heat of coking rose linearly with increasing moisture content of up to 16%, whereas for a constant moisture content for values up to 16% the heat of coking rose to a maximum for coals with about 32% volatiles and thereafter fell. Thus the lowest heat of coking was obtained in this investigation with dry coals containing 20% volatile matter and the highest value with coals of 32% volatile matter and containing 16% moisture.

Quality.—An account has appeared[95] of an investigation into the production of coke suitable for use in domestic open fires by the high-temperature carbonization of various coals in continuous vertical retorts. The suitability of a coke was mainly assessed on its initial combustibility index, which was determined by the time required for the coke to give a 'cheerful' fire radiating 5600 B.Th.U./hr. when the fire was lit under standard conditions. An improved combustibility index was obtained by steaming the retorts to increasing extents and this was particularly true when the retorts were operating at low rates of throughput. The beneficial influence was most marked when coals of relatively high rank were carbonized.

A study of the breakage of coke has been made both from the practical[96] and theoretical[97] points of view.

The urgent need for India to conserve her very limited resources of coking coals has led to an investigation[98] into the possibility of making good metallurgical coke from blends of weakly coking and more highly coking coals. It was found that only about 25% of weakly coking coal (Gray-Campredon caking index 8–12) or 35% of medium coking coal (Gray-Campredon caking index 13–14) could be incorporated in the blend. The size distribution of a blend has been shown[99] to be an important factor in the ultimate strength of the coke. Savage has reviewed[100] the question of the production of metallurgical coke and has drawn attention to the satisfactory use of coals with sulphur contents considerably higher than was acceptable a few years ago. This has become possible owing to the increasing practice of desulphurizing the iron outside the blast furnace.

A study of the variation of density of coke with the temperature of carbonization has been made by Franklin[101] who showed that the actual value obtained depended upon the medium used for its determination. Helium gave the highest values and benzene or hexane the lowest. With helium the density rose to a maximum of 2·0–2·1 g./c.c. for a carbonization temperature of 1000° c. and thereafter fell, but with benzene the density steadily approached the limiting value of 1·6–1·8 g./c.c. at temperatures above 900° c. The porous structure of coke has been examined[102] and has revealed that the pores are sufficiently small to prevent the ingress of liquids of large molecular size but large enough to permit the entrance

of small molecules. Heating to higher temperatures caused the apertures to contract and, in fact, could be made so small by heating to a sufficiently high temperature as to render the pores impenetrable to any of the liquids used in the investigation.

Radioactive sulphur in the form of iron pyrites has been added[103] to coal before carbonization in an endeavour to discover how the organic and pyritic sulphur of coal are distributed among the products of carbonization. In the early stages of carbonization the organic sulphur was found to be evolved at the greater rate, but when the carbonization was completed both forms appeared in the coke in amounts which were proportional to their original concentrations in the coal. On the other hand, Brewer and Ghosh found[104] that the total volatile sulphur increased with higher temperatures of carbonization, especially if the carbonization were effected in a current of ammonia gas. A considerable measure of desulphurization of coke could be effected by heating it in a current of ammonia.

Coking practice.—The fouling of the regenerators with solid deposits, which sometimes occurs when coke ovens are heated by gas from external producers, was found by Badger[105] to be prevented by the admission of tar oil vapours to the producer gas before it passed to the electrostatic precipitators. German coking practice has been reviewed by Reed.[106] Cassan[107] has advanced a formula for the determination of the period necessary for carbonization in coke ovens under various conditions.

Carbon.—Attempts have been described[108] to prepare carbon black by finely grinding carbonized materials such as anthracite coke and pitch coke. There appeared to be a limit to the reduction in size of particle attainable by continuously grinding these materials in a ball mill. The ground cokes were found to reinforce rubber to about the same extent as furnace carbon blacks did under similar conditions.

Low-temperature carbonization.—A study of the low-temperature carbonization of brown coal[109] showed that improved yields of coarse-grained product were obtained by pressure-drying the coal before carbonization. The effect of pressure on the low-temperature carbonization of coal has been studied.[110] At temperatures up to 500° C. higher yields of coke and gas were obtained. A description has appeared[111] of the new 'Disco' plant which is being erected at Pittsburgh at a cost of $3,000,000. The Governing Body of the Council of the Indian Board of Scientific and Industrial Research has adopted[112] the suggestion that full scale investigations of the low-temperature carbonization of India's coals should be undertaken.

Combustion

Strong support has been given to the hypothesis that carbon monoxide is the primary product of the reaction between carbon and oxygen, by a study of the effect on the reaction of certain inhibitory substances. Bridger and Appleton[113] found that the presence of certain halogen compounds (e.g. CCl_4, HCl, and Cl_2) in the air passing into a bed of burning coke brought about a marked increase in the concentration of the carbon monoxide, whereas the concentration of carbon dioxide decreased. If the concentration of the inhibitor was sufficiently high

(greater than 2·0% in the case of CCl_4) the formation of carbon dioxide was almost entirely suppressed. The increased concentration of carbon monoxide was shown not to be due to the reduction of carbon dioxide for this reaction was found to take place to only a small extent under the conditions of the experiments. It was established by further experiments that the diminution of the concentration of carbon dioxide was due to the partial suppression of the further oxidation of carbon monoxide and that 95% of the carbon monoxide could still remain unoxidized at 1000° C. in the presence of excess oxygen, provided the inhibitor was present in amounts greater than a certain critical value (about 0·5% in the case of chlorine). The question has also been discussed by Arthur and Bowring[114] particularly in relation to combustion in beds of solid fuel and also to the mechanism of fire extinction.

The combustion conditions which actually prevail inside a burning bed of solid fuel have been studied by Arthur, Bangham and Thring.[115] They found that an overwhelming proportion of the fuel was consumed within the first few particle thicknesses. Temperature measurements and gas analyses of samples taken at various points throughout the bed appeared to show that the gas acquired an increase in total energy on its passage through the bed. The most likely explanation was considered to be that the carbon monoxide, which formed the primary combustion product, burned in the voids with the surviving oxygen. The kinetics of the combustion of carbon (and coke) have also been studied by Eichner and Prettre[116] at temperatures of 1000°, 1100° and 1200° K. They found the initial reactivity of all samples to diminish with time at 1000° K. but the diminution was less at higher temperatures and disappeared entirely at 1200° K. The presence of carbon monoxide in the gas strongly inhibited the reduction of carbon dioxide below 1200° K. but this inhibitory action practically disappeared at 1200° K. The results were explained on the basis of the carbon monoxide and dioxide being absorbed on the solid combustible.

A kinetic study of the steam–carbon reaction has been made by Pilcher and Wright[117] using an apparatus which permitted the rate of reaction to be determined not only from the composition of the effluent gases, but also from the rate of loss of weight of the carbon sample which was suspended from a balance. The results of the two methods were in good agreement. Below 1100° C. the reaction was found to be highly selective and left a thick porous layer of unreacted carbon on the surface of the specimen. At 1300–1450° C. no such porous layer formed and all the material reacted. For one specimen of carbon the energy of activation over the temperature range 1000–1100° C. was 40,000–41,000 calories, while the apparent order of reaction was constant at 0·66 at 1100° C. for a range of partial pressure of water vapour of 30–360 mm.

A theoretical enquiry into the motion of carbon particles during their combustion in a stream of air has been carried out by Kontorovich.[118]

Fuel utilization

Industrial boilers.—The trends during the last ten years of American practice in steam raising have been reviewed[119] and it is evident that new plants burning oil or gas are being preferred to those burning

solid fuels. In the latter plants the spreader stoker is being used in increasing amounts. Progress in the design of mercury condenser-boilers has resulted in the reduction of the heat consumption per kwh. by 2000–2500 B.Th.U. below the heat consumption of the best steam cycle using steam pressures of 400–1200 lb./in.^{2} Details of a new installation employing mercury vapour to generate steam have been given.[120] Mercury is vaporized at 945° F. and 113 lb./in^2. and on condensation generates 200,000 lb. of steam per hour at 400 lb./in.^{2} which is used to drive a 15,000-kw. turbo-generator.

The combustion problems arising in the furnaces of boilers have been considered by Schwarz[121] who emphasized the difficulty of effecting the adequate mixing of secondary air with the burning fuel owing to the existence in most furnaces of essentially laminar flow. The limited time of travel makes diffusion and small-scale turbulence ineffective in securing satisfactory mixing, but good results can be obtained by introducing the secondary air at right angles to the burning gas column and with an equal velocity, preferably from a small number of large jets rather than from a large number of smaller ones. Kirov reports[122] that an improvement in overall boiler efficiency of 5–7% has been achieved by fitting spiral retarders to the smoke tubes of an Economic boiler thereby increasing the turbulence. A useful report by Ritchie[123] has appeared dealing with the influence of various factors on the performance of shell-type boilers.

The necessity of using high ash fuel has led to the increasing development of slagging furnaces and according to Dolezal[124] it would be possible to use fuel containing up to 80% of ash in air-cooled furnaces of this type. With water-cooled slagging furnaces there is an upper limit to the ash content of usable fuel which becomes lower as the melting point of the ash rises. Lent[125] gives the limit of ash for chain grate stokers as 45% for efficient working and 30–35% for pulverized fuel firing. Heinrich[126] has considered the design and operation of boilers with slag-tap furnaces and has stated that their efficiency is 1–3% higher than those with dry ash removal but that their cost is 8–12% higher. For this reason units giving less than about 200,000 lb. steam per hour are not regarded by him as being economic. The same author[127] has reviewed the various types of slagging furnace in use abroad. The problems of ash content, ash composition and slagging have been discussed by Grassmann.[128]

Experiences with the utilization of various types of fuel have been described: peat on a chain grate stoker,[129] lignite on a chain grate stoker,[13] slurry and coke breeze,[131] coke fines on a chain grate stoker,[132] anthracite silt,[133] bagasse on a spreader stoker.[134]

The study of bubble formation in relation to steam raising[135] has shown that the prevention of foaming depends on the generation of relatively few, large, rapidly growing steam bubbles on, or near to, the heating surface. Thus the natural tendency to form increasingly numerous small bubbles as the concentration of dissolved solids increases near the heating surface must be overcome. Certain polyamides and polyacylated polyamines are effective foam inhibitors and are thought to owe their efficacy, in part at any rate, to their being selectively adsorbed

on certain steam bubbles into which rapid evaporation takes place from adjacent water layers.[136]

Boilers cum *gas-turbines.* A description has appeared[137] of two installations in which heat is transferred from the working fluid of the turbine for the generation of steam or for the raising of the temperature of the feed water. The first extracts the heat before expansion in the turbine and the second extracts it after expansion.

Pulverized fuel firing.—Russian experiments to improve the burning of pulverized fuel have been described.[138] The introduction of deflector rings at the burner mouth enabled the furnace depth to be reduced and permitted the use of low-volatile coals. A description has appeared of a new large steam-electric generator[139] burning pulverized anthracite (85% through 200 mesh). A small amount of pulverized bituminous coal is added when necessary, e.g. when starting or when running on reduced loads, to stabilize the ignition of the anthracite. The plant incorporates a radiant-convection superheater designed for operation at 1000° F. steam temperature over a range of loads from 180,000 to 310,000 lb. steam per hour. Dolezal[140] has discussed the losses in pulverized fuel furnaces due to unburned particles of fuel, and the various causes which give rise to them. Those receiving principal consideration were connected with the ash content of the particles: (i) the actual fuel in a particle may be inaccessible to the air owing to its enclosure in a sheath of mineral matter; (ii) after partial combustion, the ash may melt and enclose the remaining unburnt fuel in an impervious envelope. The losses due to unburnt fuel are expressed by the author as a product of three functions: (*a*) of the mean ash content, (*b*) of the particle size, and (*c*) of the instantaneous boiler load. Details are given of the determination of the values of the functions. The same author[141] has discussed the design and operation of pulverized fuel furnaces burning low grade fuel. Humphreys[142] has reviewed the early developments in pulverized fuel firing and has mentioned that with the progress of the gas turbine efforts were being made to apply this type of prime mover, fired by pulverized fuel, to the locomotive field. The subject has also been reviewed by Fitton.[143]

The Stouff furnace, although not strictly a pulverized-fuel furnace, burns particles of fuel in suspension but handles granules up to 4 mm. in size. The furnace[144] is in the form of an inverted cone to which air is admitted at the bottom and fuel at a higher point. The decrease in velocity caused by the divergence of the cone causes a partial classification of the particles according to their size. The larger particles burn nearer the bottom and the smaller sizes nearer the top of the cone. Flue gases containing 12–14% CO_2 have been obtained. Installations generating 20 tons steam per hour have been built. Details of three installations have been described.[145]

Deposits and corrosion in boilers and other plant

Internal deposits and corrosion.—The corrosions of boiler tubes at the Battersea and Deptford West power stations were found to be similar in certain respects.[146] The corrosion product in the immediate neighbourhood of a deep pit was hard and laminated and consisted almost entirely

of magnetic iron oxide. Metallic copper was found between the laminations. This type of corrosion appeared to be common to a large number of stations, copper being present in the deposits. The ammonia content of the make-up water had increased appreciably during recent years and had undoubtedly contributed in no small degree to the incidence of the trouble. Long-term remedial measures will involve the partial or complete removal of ammonia from the feed water by deaeration of the raw mains water softened by zeolite base-exchange before evaporation. Young and Hall[147] have recorded the formation of barnacles in a boiler containing conditioned water by allowing it to stand cold for some time after being taken off the line. The water contained both sulphate and phosphate and both were shown to be necessary for barnacle formation. Pitting occurred beneath the barnacles whose formation was accelerated by the presence of copper salts. The desirability was emphasized of draining a boiler as soon as practicable after being removed from steam generation. Corey[148] has reviewed the problems of corrosion in high-pressure boilers particularly in relation to copper and iron oxide deposits. A study has been reported[149] of amine volatility and alkalinity in relation to corrosion control in steam heating systems.

Gillingham[150] has described recent experiments which showed that silica and certain other substances, normally non-volatile, are appreciably volatile in supercritical steam at pressures of 200 kg./cm.^{2} and over. Increased volatilities were found at higher pressures and temperatures. By virtue of its volatility in steam, silica was found to be capable of transference from water to surfaces outside. The deposits on the blades of a steam turbine were found to be of two types:[151] a soluble portion which has arisen through carbonaceous zeolite material entering the feed water of the boiler, and an insoluble portion which was largely silicic. Treatment of the boiler water with magnesium chloride almost entirely prevented the formation of deposits in both superheaters and turbines. The treatment of boiler waters containing up to approximately 200 p.p.m. silica with rusting iron shavings has been shown[152] to be an effective way of removing silica. The use of anionic exchange resins for silica removal has also been described.[153] Nonhebel[154] has reviewed the experience of many years of large-scale treatment of boiler water for high and low pressure steam generation. In a comprehensive review of their experience of the scaling of boilers Clark and co-workers[155] concluded that it was impossible to define the ratio of PO_4/SO_4 concentrations which must be conformed to in order to inhibit scaling by calcium sulphate. Identification of the constituents in a scale was secured by both microscopic examination and X-ray diffraction spectra.

The use of solvents, in particular hydrochloric and lactic acids, for the cleaning of boilers has been described[156,157] The precautions necessary to ensure their correct use have been discussed.

External deposits.—It is now agreed that the formation of SO_3 in the combustion gases is responsible for much of the deposits which occur on the gas side of boiler equipment and if means could be adopted to prevent its formation, or to effect its reduction to SO_2, the troubles due to deposits would be greatly reduced. Walsh[158] has pointed out that new boilers appear to be immune for varying periods of time depending on the

particular fuel used. This suggests that the metal surface has to undergo some change before serious troubles arise. The change might be, in part, the saturation of the metal with sulphuric acid and he recommends that all boiler surfaces be washed and neutralized at least once a year. Slag deposits were appreciably reduced after the metal had been treated with a lime slurry. Ferric oxide acts as a catalyst for the conversion of SO_2 to SO_3. The presence of sulphuric acid on a surface raises the dew point of the flue gases with which it comes into contact and causes the fly ash to adhere. The question has also been discussed by Juhasz,[159] Harlow,[160] and Crossley.[161] Whittingham[162] has recorded the observation that when silica smokes or silicon monoxide are introduced into a coal gas flame containing sulphur oxides the SO_3 is in part reduced to SO_2, with a consequent lowering of the dew point. Silicon monoxide is formed when mixtures of various silicates and carbon are heated to above 1200° c. The American practice of freezeproofing coal by additions of $CaCl_2$[163] or NaCl[164] appears likely to add seriously to the troubles due to deposits on the gas side of superheaters and economizers. The injection of superheated steam from all sides into the flames in a ship's boilers was found to be an effective way of preventing soot and slag accumulations on the heating surfaces.[165]

Work at the British Non-Ferrous Metals Research Association[166] has shown that living organisms can play a very significant part in initiating and accelerating the corrosion of condenser-tube alloys. This in some cases may be due to the formation of organic compounds, possibly containing sulphur, which act as powerful accelerators even in very small concentrations. In other cases the acceleration may be due to the formation or activation of hydrogen acceptors or oxygen carriers which affect the electrode reactions in corrosion cells. Various aspects of the fouling and cleaning of heat exchange equipment were considered[167] at a symposium on the subject.

Domestic heating and cooking.—Weston[168] has summarized the results obtained at the Building Research Station on the annual heat requirements of an average household. 20 unoccupied houses were used for the assessment, fitted with various heating systems, but the houses were well insulated and to the same extent. The trials were operated on a schedule which simulated the demands of a family of two adults and two children. It was found that at least 700 therms per annum will be required for a house of 900–950 $ft.^2$ total floor area to meet the demands of space- and water-heating. This figure is considerably higher than the estimate (292 therms) for space heating which it was considered[169] would give reasonable comfort in a house of 1000 ft^2. floor area with the traditional insulation and which it was said would be capable of reduction by one-quarter by adequate heat insulation. Some of the discrepancy might be accounted for by the experimental figure budgeting for whole-house heating. The British Standards Institution[170] has issued Chapter 7 of "Code of Functional Requirements of Buildings" which deals with heating and thermal insulation. An investigation has been reported from the Danish State Building Research Institute[171] on various aspects of heat insulation as applied to houses built according to normal Danish practice.

Chamberlain[172] has reviewed the improvements in domestic solid fuel

appliances made during recent years in this country. A circular issued by the Ministry of Health[173] contains details of the types of stoves and grates recommended as economical. Landry and Sherman[174] have described the development of a stove for the burning of bituminous coal with essentially no smoke. Research in space heaters by the U.S. Government[175] has been outlined by Tasker. The results of the testing of 150 Dutch domestic heating appliances have been given.[176]

Heat pump.—A detailed account has been published[177] of the operation of the first full-scale heat pump installation for air conditioning and heating purposes installed in this country. The plant provides services for the offices and workshops of Stourport 'B' Power Station and utilizes as its source of heat the station's condenser cooling water before its final discharge into the River Severn. The results of a two years' experimental study of a heat pump using a shallow ground coil have indicated that this type of appliance would be suitable and economic for domestic heating.[178] Sporn and Ambrose[179] have outlined the work on domestic heat pumps being carried out in America. They have expressed the opinion[180,181] that certain types are suitable economically but their high initial cost is a serious disadvantage. Griffith[182] has reviewed the problem as it applies to this country.

Underground heat storage.—Gregorig[183] has discussed a Swiss proposal to store waste industrial heat during the summer in underground water basins from which it could be drawn as required during the winter. It is estimated that a temperature drop of 10° c. would occur during storage.

District heating.—Details have been given[184] of the heating scheme which will ultimately supply 1690 flats in Pimlico, Westminster, London, with heat derived from the exhaust steam from Battersea Power Station. Ten district-heating schemes have so far been approved in England.[185] Scottish schemes include that at East Kilbride where about 10,000 dwellings and all public buildings will eventually be served. The report of the Mission to United States on district heating in American housing has been published.[186] Margolis[187] has discussed various arrangements for the source of supply of heat for district heating schemes and has commented on recent improvements. Details of schemes in Paris,[188] Klagenfurt,[189] and Gothenburg, Sweden,[190] have been given.

Large-scale hydrogenation.—A detailed discussion by Skinner and others[191] has been published of a proposed improved process of coal hydrogenation in which the overall thermal efficiency would be raised to 55%. This would represent a considerable improvement over that of a typical German plant (28·9%). The principal suggested improvements are to employ the preheating of the cold ingoing paste of coal and oil as a means of controlling the exothermic hydrogenation reaction and the adoption of a heavy oil let-down flash distillation using superheated steam.

Pulverized fuel gas-turbines.—The coal-burning gas-turbine locomotive which is being manufactured for Bituminous Coal Research Inc. has been described.[192] It will operate on an open cycle with regenerator. The six-stage reaction turbine is designed to deliver 12,243 h.p. to the turbine-compressor coupling at a speed of 5700 r.p.m. when the inlet gas temperature to the turbine is 1300° F. and the air inlet temperature

to the compressor is 70° F. and the pressure 14·7 lb./in^2. It has been announced[193] that closed- and open-cycle turbines are being developed for the burning of peat. The problem of erosion in gas turbines burning solid fuel is of vital importance to their ultimate success. A study of erosion due to fly ash has been described.[194] Ash, obtained from plants burning pulverized fuel, was allowed to impinge on a 'Vitallium' disc and was found to cause rapid erosion. When, however, the coarser particles were removed from the ash and only the finer portion used for the impingement, the target became covered with an adherent deposit which protected it from further erosion. The formation of deposit was the chief feature of impingement experiments at high temperature. Details have been published[195] of the materials used by Germany during the war for the construction of gas turbines.

'Colloidal' fuel.—Taylor[196] has reviewed the present position of coal–oil suspensions as alternative fuels to oil. Stability of the suspensions is a primary factor in their satisfactory employment and can be achieved either by the addition of stabilizers, or by the use of suitable oil as the suspending medium. Experiments have been described[197] on the use, as a Diesel fuel, of suspensions of charcoal in groundnut oil stabilized with 3% calcium soap. The maximum b.h.p. was 72·8% of that developed with mineral oil.

Atmospheric pollution

It has been estimated[198] that in 1938 British homes and industries discharged into the atmosphere about 2,400,000 tons of smoke, nearly 600,000 tons of ash and more than 5,000,000 tons of SO_2. The damage and loss caused by this pollution of the atmosphere cannot have been less than £45,000,000. The serious effects of atmospheric pollution on health are evident from the direct relationship which has been found to exist between the extent of pollution in urban areas and the death rates of pneumonia, pulmonary tuberculosis and cancer of the respiratory tract.[199] Deaths in Chicago due to these three respiratory diseases are greater in the dirtier districts than in the clean districts to the extent of 700 per annum. The oxides of sulphur in the atmosphere are responsible for considerable damage to building limestones[200] causing it to disintegrate owing to the formation of gypsum, etc. The leather bindings of books exposed to the London atmosphere have been found to contain 5% of sulphuric acid.[201] Schikorr[202] has reviewed the corrosion of metals by atmospheric impurities and has reported a study of various metals carried out at Berlin–Dahlem. The rate of corrosion was found to be dependent upon the nature and purity of the metal and the condition of its surface, but for a metal which was susceptible to attack the rate was found to be directly proportional to the content of sulphur compounds in the atmosphere and increased with rise in the dew point. Some metals were corroded rapidly at first but the rate quickly fell off owing to the formation of a protective coating on the surface of the metal. An enquiry into the possibility of danger to health and property from contamination of the atmosphere by fluorine arising from the manufacture of aluminium has been held.[203] A report of the work by the Department of Scientific and Industrial Research on atmospheric pollution has been published[204]

for the five years ending March 31, 1944. In a review of the experience at Leicester on atmospheric pollution, Richards[205] expressed the opinion that contrary to popular belief surface winds play little part in the dispersion of smoke. Smoke tends to rise quickly to the upper air where it is dispersed by the stronger winds which prevail there. Any operation such as soot blowing which produces appreciable amounts of suspended matter near the ground should therefore be carried out when atmospheric turbulence is high, i.e. in windy conditions or in the middle of the day when the sun is high.

A step of far-reaching importance was made towards the ultimate reduction of atmospheric pollution when the Minister of Health issued his request to Local Authorities asking them as far as possible to instal in their new houses no appliance burning solid fuel which had not been scheduled as efficient. A number of Authorities have obtained statutory powers, by means of Local Acts, to enforce the setting up of smokeless zones especially in the city centres.

Fuel economy

Mention has already been made in this report to matters which have a direct bearing on fuel economy. The increasing introduction of methods and appliances which permit the use of high-ash and other low-grade fuels and of devices to improve combustion and heat transfer will inevitably result in considerable economies.

Continued interest is still being shown[206,207] in the use of oxygen in blast furnace practice. Towndrow[208] has considered the question of fuel efficiency in the operation and design of blast furnaces and has presented data referring to a large modern plant. The production aspects of fuel efficiency at a large iron and steel works in this country have been presented by Stirling.[209]

A valuable contribution to the study of fuel economy was made by the Institute of Fuel[210] when it published in book form the papers on waste heat recovery from industrial furnaces which had previously been presented to a symposium held under its auspices. Considerable help will be afforded to industry in its endeavours to effect economies in fuel by the inauguration of a mobile testing service by the Ministry of Fuel and Power.[211]

The North of Scotland Hydro-Electric Board[212] has put into operation as part of its first constructional scheme two generating stations, one on the River Morar in Invernesshire and the other at Lochalsh, Rosshire. Their ultimate annual capacities will be 6 and 7 million kwh. respectively. Particulars of a further constructional scheme have been announced[213] which will necessitate the building of a dam at Loch Eigheach, whose water will provide an ultimate output of 17 million kwh./annum. The consultant engineers to the North Wales Power Company[214] have proposed six major constructional schemes and have recommended extensions to the catchment areas of the Dolgarrog and Maentwrog power stations and the installation of additional generating plant.

Analytical methods

It cannot be too strongly emphasized that the reliability of any analyical result depends, first and foremost, upon the accuracy with which the

original sample represents the bulk of the material. Manning[215] has examined the theory of coal sampling in relation to the determination of ash content. Initially the assumption was made that coal could be considered as a binary mixture of coal and dirt, but later he extended the analysis to the case of ternary mixtures of coal, middlings and dirt. He compared the weights of sample of various screen sizes required by theory to give a result of specified accuracy with the weights laid down in B.S. specifications. He found that whereas the latter required a somewhat larger weight of sample of coal, sized ½ in. or less, than was theoretically necessary, for large sized coal, 2 in. and upwards, the requirements of the specification were inadequate to give a result of specified accuracy. Bailey and Laundry[216] have examined the sampling of coal for float and sink tests.

The more important developments in the methods of analysis of solid and gaseous fuels which have occurred during the last five years have been reviewed by Gauger and Darby.[217] Details of revised American standard methods of sampling and analysis of coal and coke have appeared.[218] The methods of physical and physico-chemical examination of coal in use at the Charbonnages de France Research Station, Marienau, have been outlined by Masson.[219]

The vexed question of relating coal analyses to a mineral-matter-free basis has received consideration[220] by Himus and Basak. They found that if a coal was separated into fractions of smaller and greater ash contents than the original, there was a linear relationship between the ash content of the fractions and their contents of carbon, hydrogen, nitrogen and sulphur. If, therefore, these curves were extrapolated to zero ash content (and therefore to zero mineral matter), they gave the composition of the pure coal substance. If the general applicability of these findings is proved it will place the relationship of mineral matter to ash on a much sounder basis than has hitherto been possible.

Bainbridge *et al.*[221] have described an apparatus for the determination of moisture in brown coals by distillation with a petroleum distillate. The determination is performed more quickly than with the B.S.I. apparatus and with similar precision. A critical study of the determination of moisture in solid fuels by Simek and Ludmila[222] showed that the most satisfactory methods were either distillation with xylene or drying in a current of nitrogen at 130° c. and collecting the water in calcium chloride.

Mantel[223] has proposed an empirical formula for the calculation of the oxygen content of solid fuels:

$$0 = 1{\cdot}68 + \frac{8{\cdot}636}{100}F + \frac{2{\cdot}7273}{1000}F^2$$

where F is the volatile matter content.

Dancy and Jersey[224] have described an apparatus for the carbonization assay of coals which permits the use of only 2·5 g. of sample. The results, although mutually consistent, showed no satisfactory correlation with those of the Gray-King assay.

An examination of the C.A.B. (Critical Air Blast) test applied to anthracite and low-volatile coals has shown[225] that there is a very rapid

increase in the C.A.B. as the volatile matter of the coal diminishes below about 8%. Blends made from cokes of high and low C.A.B. gave results which departed slightly from those expected from the composition of the blend.

A method has been described[226] for the determination of the swelling pressure exerted by a coal during its carbonization.

A critical examination of the determination of calorific values has been made by Simek.[227] He has stressed the importance of the mineral matter and its associated water and has suggested methods for their determination.

References

1 *The Times*, Nov. 6, 1948
2 National Coal Board, Annual Report and Statement of Accounts for year ended December 31, 1948, H.M.S.O., 1949
3 *Hansard*, Jan. 27, 1949, **460** (47), 1095
4 *Colliery Guard.*, 1949, **178**, 221
5 H.M.S.O., 1949, Cmd. 7665
6 *Gas World*, 1949, **130**, 865
7 *The Times*, May 20, 1949
8 Ibid., Dec. 31, 1948
9 Ministry of Fuel and Power, Statistical Digest for 1946 and 1947, H.M.S.O., Cmd. 7548
10 Paper to Fourth Min. Met. Congress, Jul., 1949 ; abstract in *The Times*, Jul. 15, 1949
11 Dickinson, S. B., *Chem. Engng. Min. Rev.*, 1948, **40**, 400
12 Parkin, L. W., *S. Austral. Dept. Mines Min. Rev.*, 1948 (86), **85**, 91
13 Parker, A., ibid., 43
14 Queensland, Coordinator-General of Public Works and Kemp, J. R., Govt. Printer (Brisbane), 1947
15 *Colliery Guard.*, 1949, **178**, 590
16 *Iron Coal Tr. Rev.*, 1949, **159**, 208
17 Stockley, G. M., *Bull. imp. Inst., London*, 1947, **45**, 375
18 *S. Afr. Min. Engng. J.*, **59**, Pt. 2 (2918), 597
19 Harrington, H. J., Wellington, New Zealand: D.S.I.R., Coal Survey Comm., Coal Survey Report No. 181, Jul. 4, 1947
20 Idem, ibid., No. 185, Oct. 3, 1947
21 Willett, R. W., *N.Z. J. Sci. Tech.*, 1948, **29** B, 228
22 Canada, Dept. Mines and Resources, 1947
23 Lang, W. A., *Trans. Canad. Inst. Min. Met.*, 1949, **52**, 15; *Canad. min. metall. Bull.*, 1949, **42**, 17
24 Karunakaran, C., Narasinga-Rao, M. and Subbiah, R., *Curr. Sci.*, 1948, **17**, 260
25 Fieldner, A. C., *Oil Gas J.*, 1949, **47**, 138, 142, 145
26 Young, W. H., Anderson, R. L. and Hall, E. M., U.S. Bur. Mines Mineral Ind. Survey, 1948, Mineral Market Report M.M.S., No. 1664
27 Hsieh, C. Y., *Econ. Geol.*, 1949, **44**, 128
28 Budryk, W., *Przeglad Gorniczy*, 1949, **5** (3), 253
29 Wolpert, V., *Min. J.*, 1949, **232**, 490
30 Baty, V., *Ann. Mines Belg.*, 1949 ; abstract in *Colliery Guard.*, 1949, **179**, 205
31 Toenges, A. L., Kelly, L. W., Davis, J. D., Reynolds, D. A., Fraser, T., Crentz, W. L., and Abernethy, R. F., U.S. Bur. Min., 1949, Bull. No. 474
32 *Canad. Min. J.*, 1949, **70**, 93
33 *Ann. Min., Paris*, 1948, **137** (11), 51
34 *The Times*, May 21, 1949
35 Thiergart, F., *Z. Dtsch. geol. Ges.*, 1945, **97**, 54
36 Petrascheck, W., *Sitzb. Oesterr. Akad. Wiss., Math.-Naturwiss, Kl.*, **156**, Pt. 1 (7–8), 375
37 Bond, R. L., Griffith, M. and Maggs, F. A. P., *Discuss. Faraday Soc.*, No. 3, 1948, 29
38 Dresel, E. M. and Griffith, M., *Fuel, Lond.*, 1949, **28**, 193
39 Franklin, R. E., *Trans. Faraday Soc.*, 1949, **45**, 274, 668
40 Brusset, H., *Bull. Soc. Chim. Belg.*, 1948, **57**, 373

[41] Reynolds, F. M., *J. Soc. chem. Ind.*, 1948, **67**, 341
[42] Katchenkov, S. M., *Doklady Akad. Nauk U.S.S.R.*, 1948, **61**, 857
[43] Simek, B. G., Coufalik, F. and Stadler, A., *Zpravy Ustavu Vedecky Vyzkum Upli*, 1948, 167
[44] Mason, B., *J. Geol.*, 1949, **57**, 62
[45] Jones, R. E. and Townsend, D. T. A., *J. Soc. chem. Ind.*, 1949, **68**, 197
[46] Busch, H. W., Berger, L. B. and Schrenk, H. H., U.S. Bur. Min., Rep. Invest., 4465, 1949
[47] Friedman, L. D. and Kinney, C. R., Paper to Div. Gas Fuel Chem., Amer. Chem. Soc., Sep., 1948
[48] Kiebler, M., U.S.P. 2,461,740
[49] Belcher, R., *J. Soc. chem. Ind.*, 1948, **67**, 213, 217, 218
[50] Ahmed, M. D. and Kinney, C. R., Paper to Div. Industr. Engng. Chem., Amer. Chem. Soc., Washington, 1949
[51] Polansky, T. S. and Kinney, C. R., Paper to Div. Petrol. Chem., Amer. Chem. Soc., Sep., 1948
[52] Charmbury, H. B., Herbert, S. A. and Kinney, C. R., Paper to Amer. Chem. Soc., Apr., 1948
[53] Orchin, M., Goldbach, G. L., Wolak, M. and Storch, H. H., U.S. Bur. Min. Rep. Invest. 4499, 1949
[54] Glenn, R. A., *Fuel, Lond.*, 1949, **28**, 32
[55] Sato, F., Morikawa, R., Okamura, T., and Oda, K., *J. Soc. chem. Ind., Japan*, 1942, **45**, 892
[56] Dryden, I. G. C., *Nature*, 1949, **163**, 141
[57] Idem, *B.C.U.R.A. Mon. Bull.*, 1949, **13**, 113
[58] D'Yakova, M. K. and Davtyan, N. A., *J. appl. Chem., U.S.S.R.*, 1948, **21**, 113
[59] Frese, E., Board of Trade German Div. Doc. Unit, F.D. 940/49
[60] Berkowitz, N., *Nature*, 1948, **162**, 960
[61] Boyd, J., *Min. Congr. J.*, 1948, **34** (6), 26, 31
[62] Terrell, W. A., Paper to South Western Soc. Min. Engrs., Oct. 9, 1948; *Colliery Guard.*, 1948, **177**, 845
[63] East, J. H. and Maize, E. R., Amer. Inst. Min. Met. Engrs., Tech. Publ. No. 2384, Class A; *Min. Technol.*, 1948, **12** (4), 8 pp.
[64] Elliott, M. A., U.S. Bur. Min., Rep. Invest. 4381, 1948
[65] Alcock, J., Paper to Midland Inst. Min. Engrs., May 5, 1949; *Colliery Guard.*, 1949, **178**, 715
[66] Winkhaus, G. P., *Glückauf*, 1948, **84**, 707
[67] *Engineer, Lond.*, 1948, **186**, 435
[68] Miles, E., *Iron Coal Tr. Rev.*, 1948, **157**, 293
[69] *Min. J.*, 1948, **231**, 549
[70] *Colliery Engng*, 1949, **26**, 176
[71] Vidal, V., *Rev. Industr. min.*, 1948; *Colliery Guard.*, 1949, **178**, 714
[72] Liège: Inst. Nat. Industr. Charbonnière, Bull. No. 4, 1949
[73] Lidin, G. D., *Ugol*, 1948, **9**, 270
[74] Jablecki, W., *Przeglad Gorniczy*, 1949, **5**, 304
[75] Schultze-Rhonhof, D. H. and Klinger, K., Essen: Glückauf, G.m.b.H., 1948; review in *Glückauf*, 1949, **85**, 278
[76] Snyder, R. H., *J. Amer. Wat. Wks. Ass.*, 1947, **39**, 751
[77] Dahlgren, E. G., *Gas (Los Angeles)*, 1949, **25**, 40
[78] Minchin, L. T., *Gas World*, 1948, **129**, 931
[79] *Colliery Guard.*, 1949, **178**, 27
[80] Hay, P. S., Paper to Internat. Congr. on Industr. Med.; abstr. in *Colliery Guard.*, 1948, **177**, 444
[81] Rolshoven, H. and Heitmann, A., *Glückauf*, 1949, **85**, 179
[82] Heppleston, A. G., *Bull. Instn Min. Metall*, 1949, No. 511, 9; *Trans. Instn. Min. Engrs., Lond.*, 1949, **108**, 456
[83] King, E. J., Society of Chemical Industry Conference, 'Dust in Industry,' **1948**, 141
[84] Janssens, P. G. and Gandibleux, M., *Rec. Trav. sci. méd., Congo Belge*, May, 1946 and Jul., 1947 (5), 1; (6), 81
[85] Hurysz, Y., *Przeglad Gorniczy*, 1949, **5**, 32
[86] Fire Protection Ass. Tech. Booklet No. 2, Revised Ed.; *Gas Times*, 1949, **58**, 217
[87] Ohio Coal Association, Division of Engineering and Research; Review in *Coal-Heat*, 1949, **55**, 45

[88] Teissier, P., *Mines*, 1948, **1**, 23
[89] Swartzman, E., *Trans. Canad. Inst. Min. Met.*, **1949**, **52**, 117; *Canad. Min. Metall. Bull.*, 1949, **42**, 272
[90] Voznyi, G. E., *Stal*, 1947, **7**, 1062
[91] Day, R. J. and Wright, C. C., Penn. State Coll. Min. Industr. Exptl. Stn., 1948, Tech. Paper, 139; Amer. Inst. Min. Engnrs. Tech. Publ. 2429
[92] Muloey, P. A. and Eckerd, J. W., Trans. 5th Annual Anthracite Conference, Lehigh Univ., May, 1947, 155
[93] Foureau, P., *Combustible*, 1947, **20**, 38
[94] Tettweiler, R., *Gas-u. Wasserfach*, 1949, **90**, 25, 68, 73
[95] Rhead, T. F. E. and Pickering, E. T., *Inst. Gas Engnrs.*, 1948, Comm. 343
[96] Taylor, V. T. and Hebden, D., Paper to Instn. Gas Engnrs., Nov., 1948; Gas Res. Bd., 1948, Comm. 42
[97] Epstein, B. and Lowry, H. H., Carnegie Inst. Technol., Coal Res. Lab. Contrib., 147, 1948
[98] India, Council of Scientific and Industrial Research, 1948, Fuel Res. Comm. Rep. No. 2
[99] Czyzewski, M. and Byrtus, F., Prace Badawcze Glownego Inst. Met. i Odlewnictwa (Rep. Met. Foundry Res. Inst.), No. 1, 1949, 73
[100] Savage, P. S., Paper to Eastern States Blast Furnace Coke Oven Ass., Feb. 11, 1949; abstr. in *Blast Furn.*, 1949, **37**, 323, 324, 334
[101] Franklin, R. E., *Bull. Soc. chim. Fr.*, 1949, D53
[102] Bond, R. L. and Maggs, F. A. P., *Fuel, Lond.*, 1949, **28**, 172
[103] Eaton, S. E., Hyde, R. W. and Old, B. S., *Metals Technol.*, 1948, **15**, Tech. Publ. 2543
[104] Brewer, R. E. and Ghosh, J. K., Paper to 114th Meet. Amer. Chem. Soc., Sep., 1948; abstr. in *Amer. Gas J.*, 1948, **169** (3), 37; *Gas Times*, 1948, **57**, 148
[105] Badger, E. H. M., Paper to Society of Chemical Industry Conference, 'Dust in Industry,' **1948**; *Chem. Age*, 1948, **59**, 447
[106] Reed, F. H., U.S. Bur. Min., 1948, Inform. Circ. 7462
[107] Cassan, H., *Chal. et Industr.*, 1948, **29**, 292
[108] Bremner, G. M. and Colpitts, J. H., *Trans. Instn. Rubb. Ind.*, 1948, **24**, 35
[109] Simek, B. and Ludmila, J., *Paliva a Voda*, 1949, **29**, 33
[110] Simek, B. G., Ludmila, J. and Edinger, J., ibid., 97
[111] *Coke*, 1948, **10**, 386
[112] *Chem. Tr. J.*, 1949, **124**, 456
[113] Bridger, G.W. and Appleton, H., *J. Soc. chem. Ind.*, 1948, **67**, 445
[114] Arthur, J. R. and Bowring, J. R., *J. chem. Soc.*, **1949**, Suppl. Issue No. 1, S1
[115] Arthur, J. R., Bangham, D. H. and Thring, M. W., *J. Soc. chem. Ind.*, 1949, **68**, 1
[116] Eichner, C. and Prettre, M., *Mém. Serv. Chim. État*, 1945, **32**, 240
[117] Pilcher, J. M. and Wright, C. C., Paper to Amer. chem. Soc., Div. Gas Fuel Chem., Sep., 1948; abstr. in *Petroleum*, 1949, **12**, 49
[118] Kontorovich, B. V., *Bull. Acad. Sci., U.S.S.R.*, Sect. Tech. Sci., 1948, 1079
[119] Brown, C. O., *Times Rev. Ind.*, 1949, **3** (30), 20
[120] *Mech. Engng., N.Y.*, 1949, **71**, 243
[121] Schwarz, K., *Brennstoff, Waerme, Kraft*, 1949, **1**, 45
[122] Kirov, N. Y., *J. Inst. Fuel*, 1949, **22**, 192
[123] Ritchie, E. G., Rep. Shell-Type Boiler and Firing Equipment Comm. (R/16); Brit. Coal Util. Res. Ass., Mar., 1948
[124] Dolezal, R., *Technik*, 1947, **5**, 246, 274
[125] Lent, H., Rep. No. 2/3, Vereinigung der Grosskesselbesitzer, 1948, 32
[126] Heinrich, K., Rep. No. 1, Vereinigung der Grosskesselbesitzer, 1948, 2
[127] Idem, Paper to Vereinigung der Grosskesselbesitzer; abstr. in *Combustion*, 1949, **20**, 43
[128] Grassmann, *Technik*, 1948, **3**, 339
[129] Bartel, F., Rep. No. 1, Vereinigung der Grosskesselbesitzer, 1948, 41
[130] Gibson, G. E., *Power*, 1948, **92**, 98
[131] *Coke*, 1948, **10**, 315
[132] Dobson, W. E., Paper to Midland Jun. Gas Assocn., Feb. 22, 1949; abstr. in *Gas World*, 1949, **130**, 452, 453
[133] Otto, H. H., Wilson, V. H. and Dennen, W. L., Trans. 5th Ann. Anthracite Conf., Lehigh Univ., May, 1947, 269
[134] Meissner, H. G., *Combustion*, 1948, **20** (3), 44

[135] Gunderson, L. O. and Denman, W. L., *Ind. Eng. Chem.*, 1948, **40**, 1363
[136] Jacoby, A. L. and Bischmann, L. C., ibid, 1360
[137] *Engng. Boil. Ho. Rev.*, 1949, **64**, 272, 283
[138] Lyachovski, D. N., Kotloturbostroenie (Boiler and Turbine Manuf.), 1949 (2), 18; abstr. in *Engng. Boil. Ho. Rev.*, 1949, **64**, 246
[139] Schueler, L.B. and Weismantle, A. R., *Pwr Genern.*, Dec., 1948, **32**, 54, 126
[140] Dolezal, R., *Strojn. Obz.*, 1947, **27**, 168
[141] Idem, Transl. from Czech in *N.Z. Engng.*, 3 (9), 868; abstr. in *Pwr Wks. Engng.*, 1949, **44**, 128
[142] Humphreys, C. G. R., *Combustion*, 1948, **20** (3), 34; (4), 44; (5), 40
[143] Fitton, A., *Inst. Petrol. Rev.*, 1949, **2**, 18
[144] *Engng. Boil. Ho. Rev.*, 1949, **64**, 228
[145] Stouff, L., *Chal. et Industr.*, 1949, **30**, 41
[146] Rees, R. L. and Howes, E. A., Amer. Soc. Mech. Engnrs., Paper No. 48-A-100, to Ann. Meet., Nov. 29–Dec. 3, 1948
[147] Young, R. S. and Hall, A. J., *Combustion*, 1949, **20** (7), 41
[148] Corey, R. C., *Amer. Soc. Test. Mat. Proc.*, 1948, **48**, 907
[149] Berk, A. A. and Nigon, J., U.S. Bur. Min., Tech. Pap. 714
[150] Gillingham, T. E., *Econ. Geol.*, 1948, **43**, 241
[151] Long, F. H. and Pollock, W. A., Paper to Amer. Soc. Mech. Engrs., 1948; abstr. in *Mech. Engng., N.Y.*, 1948, **70**, 694
[152] Leaf, W. B., *J. Amer. Wat. Wks. Ass.*, 1948, **40**, 980
[153] Rayet, R., Paper to XXI Congr. de Chim. Industr., Bruxelles, Sept., 1948; abstr. in *Chim. et. Industr.*, 1948, **60** (3 bis), 64
[154] Nonhebel, G., *J. Inst. Fuel*, 1949, **22**, 140
[155] Clark, L. M., Gerrard, W. F., Hunter, E., Bunn, C. W., Alcock, T. C. and Thurston, E. F., *J. Soc. chem. Ind.*, 1938, **57**, 295, 298, 301; Collected and reprinted by I.C.I. Ltd.
[156] *Heat Engng.*, Oct., Nov. and Dec., 1948, **23**, 78
[157] Kilsby, E. R., *Pwr Genern*, Jan., 1949, **53**, 69
[158] Walsh, E. F., Amer. Soc. Mech. Engrs., Paper No. 49-S-19, to Spring Meet., May 2-4, 1949
[159] Juhasz, S., *Tekn. Tidsskr.*, 1949, **79** (4), 49
[160] Harlow, W. F., Paper to Extra Gen. Meet. Instns. Mech. Engrs. and Elect. Engrs, Mar. 4, 1949; *J. Inst. Mech. Engrs.*, Feb., 1949
[161] Crossley, H.E., Paper to Instn. Chem. Engrs., Dec. 14, 1948; abstr. in *Chem. and Ind.*, **1949** (2), 27
[162] Whittingham, G., *J. Soc. chem. Ind.*, 1948, **67**, 411
[163] *Coal-Heat*, 1948, **54** (4), 66
[164] *Pwr Genern.*, Sep., 1948, **52**, 74
[165] *Mar. Engng. Shipp. Rev.*, 1949, **54**, 63, 78
[166] Rogers, T. H., *J. Inst. Met.*, 1948, **16**, 19
[167] Collins, L. F., Webb, W. L., Clapper, R. L. and Armstrong, R. M., Amer. Soc. Mech. Engrs., Paper No. 48-A-137, to Ann. Meet., Nov. 29–Dec. 3, 1948
[168] Weston, J. C., *J. Inst. Fuel*, 1949, **22**, 133
[169] Ministry of Works, Post War Building Studies, No. 25, H.M.S.O., 1948
[170] Brit. Stand. Instn, 1949, Code of Practice C.P.3, Chap. VII
[171] Becher, P. and Danish State Building Research Institute, Copenhagen, The Institute, Rep. No. 1, 1949
[172] Chamberlain, E. A. C., *Coke*, 1949, **11**, 139
[173] Ministry of Health, 1948, Circ. No. 170/1948
[174] Landry, B. A. and Sherman, R. A., Paper to Ann. Meet. Amer. Soc. Mech. Engrs., 1948, No. 48-A-119
[175] Tasker, C., *Heat. Vent. Engr.*, 1949, **22**, 601
[176] Beek, F. van, Nijverheidsorganisatie T.N.O. Inst. voor Warmte-Economie, Rep. No. 4, 1949
[177] *Industr. Heat Engr.*, 1949, **11**, 164
[178] Coogan, C. H., Edison elect. Inst. Bull.; abstr. in *Heat Pip. Air Condit.*, 1949, **21**, 110
[179] Sporn, P. and Ambrose, E. R., *Heat. & Ventilating*, 1949, **46** (5), 80
[180] Idem, ibid. (2), 78
[181] Idem, *Elect. World, Lond.*, 1949, **131**, 66, 151
[182] Griffith, M. V., *Brit. Sci. News*, 1949, **2** (15), 74

[183] Gregorig, R., *Schweiz. Bauztg*, 1948, **66**, 599
[184] *The Times*, Sep. 10, 1949
[185] Smith, D. V. H., Paper to Ann. Conf., Nat. Smoke Abatement Soc., Sept. 30–Oct. 1, 1948; abstr. in *Iron Coal Tr. Rev.*, 1948, **157**, 951
[186] Ministry of Fuel and Power, Nat. Building Studies, Spec. Rep. No. 7, H.M.S.O., 1949
[187] Margolis, A. E., Paper to Public Health and Municipal Engng. Congr., Nov. 18, 1948; abstr. in *Industr. Heat. Engr.*, 1949, **11**, 1
[188] Theodore, J., *Énergie*, 1948, **32** (51), 235
[189] Triplat, E., *Elektrotech. u. Maschinenb.*, 1948, **65**, 165
[190] *Air Treatment Engr.*, 1949, **12**, 208, 240, 242
[191] Skinner, L. C., Dressler, R. G., Chaffee, C. C., Miller, S. G. and Hirst, L.L., *Ind. Eng. Chem.*, 1949, **41**, 87
[192] Tucker, W. B., Paper to semi-annual meeting of Amer. Soc. Mech. Engrs., May 30–June 5, 1948, Milwaukee, Wis.; abstr. in *Mech. Engng., N.Y.*, 1948, **70**, 877
[193] *The Times*, Oct. 10, 1949
[194] Fisher, M. A. and Davis, E. F., Amer. Soc. Mech. Engrs., Paper No. 48-A-53, at Ann. Meet., Nov. 29–Dec. 3, 1948
[195] Adderley, J. W., BIOS Overall Rep. No. 12, H.M.S.O., 1949
[196] Taylor, R. A. A., *Inst. Petrol. Rev.*, 1949, **3** (27), 83
[197] Verman, L. C., Nair, K. A., Khanna, M. L. and Dasgupta, S. K., *Gas Oil Pwr*, 1948, **43**, 330
[198] *The Times*, Nov. 22, 1948
[199] Mills, C. A. and Mills-Porter, M., *Occup. Med.*, 1948, **5**, 614
[200] Camerman, C., *Ann. Inst. Tech. Bâtiment et Trav. Publ.*, 1948, **14**, 1; abstr. in *Chim. et Industr.*, 1948, **60**, 581
[201] Innes, R. F., *Smokeless Air*, Autumn–Winter, 1948 (68), 23
[202] Schikorr, G., *Arch. Metallk.*, 1948, **2** (7), 223
[203] Agate, J. N., Bell, G. H., Boddie, G. F., Bowler, R. G., Buckell, M., Cheesman, E. A., Douglas, T. H. J., Druett, H. A., Garrad, J., Hunter, D., Perry, K. M. A., Richardson, J. D. and Weir, J. B. de V., Med. Res. Council, Memo. No. 22, H.M.S.O., 1949
[204] Dept. Sci. Industrl. Res., H.M.S.O., 1949
[205] Richards, S. H., Paper to 115th Nat. Meet., Amer. Chem. Soc., 1948; abstr. in *Chem. Age*, 1949, **60**, 520
[206] Grison, M., *Métallurgie*, 1948, **80**, 25, 29, 31
[207] Publications Inst. Recherches Sidérurgie, 1948, Ser. A, No. 2
[208] Towndrow, R. P., *J. Inst. Fuel*, 1949, **22**, 222
[209] Stirling, A., ibid., 166
[210] Institute of Fuel, 1948, 'Waste-heat Recovery from Industrial Furnaces' (Chapman and Hall)
[211] *Iron Coal Tr. Rev.*, 1948, **157**, 1272
[212] *Engineering*, 1948, **166**, 615
[213] Scottish Home Dept., H.M.S.O., 1949, Cmd. 7683
[214] *Engineering*, 1948, **166**, 639
[215] Manning, A. B., *Fuel*, 1949, **28**, 49
[216] Bailey, A. L. and Landry, B. A., *Min. Engng.*, 1949, Sect. Trans., Tech. Publ. 2539F, 79
[217] Gauger, A. W. and Darby, H. T., *Analyt. Chem.*, 1949, **21**, 227
[218] 1948 Suppl. to Book of A.S.T.M. Stand. incl. Tentat., Pt. III-A, 1949, A.S.T.M.: D271–48; A.S.A.: K 18.1–1948, 9–35
[219] Masson, R., Communic. 66th Congr. Ass. Tech. Industr. France, 1949; abstr. in *Circ. Bibl. Ass. Tech. Industr. Gas*, Jul. 15–Aug. 15, 1949
[220] Himus, G. W. and Basak, G. C., *Fuel, Lond.*, 1949, **28**, 57
[221] Bainbridge, J. R., Scanlan, P. G. and Belyea, I., ibid., **28**, 88
[222] Simek, B. G. and Ludmila, J., *Contr. Coal Res. Inst.*, Prague, 1948, **4**, 263
[223] Mantel, W., *Brenn.-Chem.*, 1949, **30**, 92
[224] Dancy, T. E. and Jersey, N. J. de, *Fuel, Lond.*, 1949, **28**, 109
[225] Kreulen-van Selms, F. G. and Kreulen, D. J. W., ibid., 29
[226] Kushnirevich, N. R., *Zavodskaya Lab.* (Factory Lab.), 1947, **13**, 325; abstr. in *Chem. Abs.*, 1948, **42**, 9121
[227] Simek, B. G., *Chem. listy*, 1944, **38**, 141; *Communic. Coal Res. Inst., Prague*, 1948, **4**, 349

GAS AND DESTRUCTIVE DISTILLATION

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THE Parliamentary reactions described in previous Reports[1] have gone nearly to completion. Most of the coke ovens owned by colliery interests have now been for three years under the control of the National Coal Board; the gas industry was nationalized on May 1, 1949; the steel industry reaction is, however, not yet complete. It is becoming inappropriate to refer to 'The By-Product Coking Industry' since by-product coke ovens, divided between the gas industry, the coal industry, and the steel industry, are taking their place as a method of carbonization to be adopted by any one of these three industries when circumstances make it desirable to use that particular form of carbonizing plant, and a common policy on the part of owners of these plants will become increasingly difficult.

The nationalized gas industry follows the general administrative pattern suggested in this Report last year.[2] The country has been divided into 12 areas each under the control of an Area Board. The Chairmen of these Boards, together with an independent Chairman and Deputy Chairman constitute the Gas Council. This Council advises the Minister on questions affecting the gas industry and is charged with the task of promoting and assisting the efficient exercise and performance by the Area Boards of their functions. In most respects the Area Boards are autonomous and the Gas Council can act on their behalf only if authorized by them to do so. This form of administrative arrangement is generally considered to be better than that of any other nationalized fuel industry since it avoids over-centralization. The Area Boards must furnish to the Gas Council at its discretion full information as to their several activities and finance, in order that the Gas Council can exercise general advisory supervision and in the last resort advise the Minister if any Area Board appears to be in difficulty or inefficient. The Gas Council is charged with the duty of settling, in consultation with the Minister, programmes of research and of seeing that those programmes are put into effect. It must ensure that Area Boards undertake the training and education of their staff. The Act requires the National Coal Board and the Area Gas Boards to co-ordinate their carbonization activities, and it is intended in this way to avoid waste of coke oven gas, over-production of coke and other forms of wastage of the national resources of coal; also, the available plant and labour should be more effectively employed. A joint committee has been set up during the year, representing the Gas Council and the N.C.B. Carbonization branch in order to implement this requirement of the Act.[3]

Whatever the difficulties that existed in the past in the maintenance of gas undertakings in a state of technical efficiency, they should be removed through the operation of efficient Area Boards having adequate financial sums at their disposal to build new plants, or to put old ones

into a thorough state of repair, wherever necessary and desirable. Generally the pre-nationalized gas industry was highly efficient, even though its works suffered, as in all elderly industries, from unplanned growth. There have been found, however, some places where conditions were bad enough to cause the Deputy Chairman of the Gas Council, Col. H. C. Smith,[4] to describe them as 'shocking.' The technical development of the gas industry should therefore be improved as a result of nationalization—if the Treasury allows adequate capital expenditure. The opinion is expressed in many quarters that Area Boards must avoid even the modest amount of centralization that would result from too rigid control of such large areas from the centre.

Policy and fuel reserves

The need for a national fuel policy is no less clamant now that the nationalization reaction has proceeded nearly to completion. It is recorded in last year's Report that the Minister of Fuel and Power had stated that it would not be possible to proceed with a long-term policy of co-ordination in national fuel matters until all the major fuel industries had been nationalized[5]; nothing published during 1949 suggests that this function of the Ministry of Fuel and Power is to be performed.

Much interest has been taken during the year in world reserves of fuel. M. King Hubbert[6] has shown that, measured by the past and probable future existence of the human race, the period during which fossil fuel will be available for our use is extremely short and a phenomenal rise in human population has coincided with the period during which fossil fuels have been used. A. Parker[7] estimates that there is only enough realizable solid fuel in the world to last for 1000–2000 years and that oil and natural gas may well be exhausted in 50–100 years. The problem of finding alternative sources of energy thus faces scientific and technical men the world over. The long-term problem is that of the survival of the human race after this period of coal utilization has ended. The short-term problem facing certain countries, of which Britain is one, is that of obtaining energy from other sources than coal and at a price that will be comparable with those ruling in coal-using nations, within a much shorter period after which the coal reserves of these countries will be exhausted. Britain has probably only 150–200 more years to solve this problem.

A problem of immediate significance is that of producing coke and gas when the first-class coking and gas coals with which Britain has been liberally supplied in the past are exhausted. The work of the Coal Survey has shown that the best coking coals will be exhausted within perhaps 40 or 50 years and the operations of the N.C.B. have shown that the mining of these coals frequently involves considerable mining losses.[8] The gas industry is disturbed by the growing shortage of good gas coals that may become acute within a few years. Much of the research work of these two branches of the carbonizing industry is directed to the use of less highly coking coals for the purpose of the manufacture of metallurgical coke and of town gas. The British Coking Industry Research Association has been actively engaged on these and other problems during the year. An event of considerable importance has

been the occupation by the Gas Research Board of its own premises and laboratories at Beckenham.

Coking properties of coal

In view of the need to use coals of inferior coking power for the manufacture of furnace coke, attention may again be turned to fundamental work on the coking properties of coal. N. Berkowitz[9] has concluded that the presence of a fusible component in coking coals is not the cause of their possession of coking properties. It is suggested that a satisfactory explanation of coking can be obtained from a consideration of the physical structure of bituminous coals, softening and thermal swelling being due to the mobility of 'micelles' and to the pore structure of coals respectively; if this were true the chemical constitution of the coal would be of only minor importance in connexion with its coking properties. This view is not supported by H. Mainz and H. Schwarzmann[10] who confirm the generally accepted view of the nature of the swelling of coal during coking and the pressure exerted in consequence. The seat of the swelling was found to be in the bright constituents of the coal whereas the dull constituents were characterized by considerable shrinking in volume. J. G. King[11] has pointed out that the quantity of material extracted from coking coals by solvents cannot be correlated directly with the coking properties of those coals; work at the Fuel Research Station has shown that one of the most important factors in coking appeared to be the physical state of the infusible portion of the coal. It is very probable that if a coal is to possess coking properties it must contain a proportion of material which under the conditions of carbonization will become fluid or semi-fluid and will set up the condition known as 'plasticity'; it may well be significant that considerable internal pressures occur in the plastic layer. King referred to the observation made at the Fuel Research Station[12] that bituminous coal when heated with hydrogen under pressure liquefies at about 350° C. during the early stages of hydrogen attack. If the reaction is interrupted at this point, the product solidifies to a pitch-like material of phenomenally high caking power. This may be an observation of special interest in connexion with the problem of using coals of inferior quality for carbonization since this highly-caking material can be produced also from non-caking coals and if a portion of the (poorly-caking) coal that it is desired to use could be partially hydrogenated by the agency of the end gases of carbonization which are rich in hydrogen, the resulting highly-caking material could then be blended with the bulk of the coal.

Work on the effect of swelling pressures on oven walls was described in the ANNUAL REPORTS last year.[13] F. Wehrmann[14] has indicated that among the precautions taken in Germany are the mixing of swelling coals with non-swelling coals and timing the maximum swelling in the central parts of the oven to coincide with shrinkage of the charge in the outer zones. Proper grinding of the coal and temperature control are also said to be effective. High flue temperatures, causing increased temperature gradients, may result in the shrinking phase starting too late to compensate for the swelling. Particular care is needed with narrow ovens. A volatile content of 23–24% is considered the limiting figure between swelling and non-swelling coals. Westphalian coal of 24% V.M. was

coked successfully in wide oven chambers at 1100–1200° C., but when used in vertical ovens at 1300° C. it gave difficulties owing to swelling pressures.

Low-temperature carbonization

Very little appears to have been published on low-temperature carbonization during the year under review. Disregarding the question of whether it is desirable or not that coal should be carbonized at a low temperature for the manufacture of the specific products obtained from this process, it is likely that national ownership of coal will remove all incentive on the part of private individuals to investigate such methods of carbonization. The Disco plant at Pittsburgh, which was mentioned last year as being the largest low-temperature carbonization plant in the world, is now in full production.[15]

Coke-oven practice

The carbonization problems that face the National Coal Board have been discussed by L. O'Connor.[16] The coke ovens taken over by the N.C.B. comprise 41% of the coking capacity of the country and in 1948 these N.C.B. plants produced 6,320,000 tons of coke, 36,917 million cu. ft. of gas for sale, 24,500,000 gal. of crude benzole, 66,750 tons of sulphate of ammonia and 339,000 tons of crude tar. Many of these plants are nearing the end of their useful lives and in order to maintain output of coke at present levels it is estimated that between £20 million and £25 million would have to be spent over the next five years. The high capital cost of coking plant makes it very difficult to rebuilding existing plants if they are to continue to operate at a profit. R. J. Barritt[17] has pointed out that for this reason new coking plants must be considerably larger in capacity than most existing plants, probably of the order of 1500 tons of coal carbonized a day, and that since very few collieries can provide this quantity of slack either the mining programme must be adjusted in order to provide this quantity of coking coal from selected collieries or the coking plant must be centralized to take its coal supplies from several neighbouring collieries. Such a policy carried out all over the country would mean that existing N.C.B. coke production would be concentrated in two-thirds of the 54 plants taken over by the N.C.B. on vesting date. The cost of transmission of gas and coke to the consumer probably necessitates situating plants within 15–20 miles of the area of major consumption.

Fears that the coke supply would be insufficient to provide for the immediate future requirements of the iron and steel industry are understood to have been removed through the operations of a Committee set up by the Ministry of Supply and presided over by Sir Ernest W. Smith[18]; it had been found that the output of existing ovens could be considerably increased and that certain constructional repair work now in hand could be speeded up. The long period that now elapses between placing an order and completion of a plant enhances the difficulties of maintaining coke supplies in view of the physical condition of many of the older coke oven plants. All new N.C.B. plants are to be properly equipped to blend coal satisfactorily[16]; in the present state of knowledge blending of more highly coking coals with those of poorer coking quality seems to be the only practical method of producing good metallurgical coke from many

coals that are now being carbonized, but the cost of blending is considerable on account of the transport costs involved in bringing highly coking coals from a distance.

A distinction must be made between blending and mixing, and this is all the more necessary since much 'blending plant' is capable of doing no more than mixing. J. Meissner[19] considers that a specially designed plant should be used for blending for the production of metallurgical coke and suggests for this purpose 'bed blending,' in which the several varieties of coal are stacked in horizontal layers by use of a belt conveyor and tripper, whereby a relatively small quantity of material is scattered evenly along the bed with each forward and backward pass of the tripper, the pile being built up to a considerable height. In the reclaiming operation nearly vertical slices are cut through the layers and a small portion is removed from every layer for each of hundreds of slices. Since wind and weather may interfere with this operation if conducted in the open, in modern American practice blending vaults are used, served by a distributing conveyor and tripper, and having mechanical means for removing the blended coal to the disintegrators.

The increasing use of froth flotation for cleaning fine coals, often followed by thermal drying, is assisting materially in reducing the ash content of metallurgical coke,[17] but may create difficulties from deterioration of coke quality when the coal contains much fusain or is easily oxidizable. Many existing coking plants supply special cokes, e.g. for foundry work or electrode carbon, and being small can only make a profit by reason of the higher prices secured; quality is therefore of the highest importance and the whole colliery and washery policy should be subordinated to the need for supplying the special high grade of coal required.

The relationship between coke-oven dimensions and coke quality has been investigated by a sub-committee of the British Coke Research Association.[8] It is concluded that the quality of coke is determined principally by the characteristics of the coal from which it is produced; wider ovens produce a greater proportion of large-sized coke, but the variation of the width between 16 and 19 in. and of the height between 10 and 15 ft. does not affect the shatter and abrasion indices with the same carbonization rate; increase in carbonizing rate decreases both the size of the coke produced and the shatter index, while fine grinding increases the shatter index. Within a given coalfield, increase in B.S. swelling number above 5 or 6 is not necessarily associated with an increase in shatter or abrasion indices, and in consequence it appears that the best use of the highly swelling coals is as materials for blending with coals of lower swelling indices.

General post-war developments in plant design have been discussed by D. Hicks and G. W. Lee.[8] Older British coking plants are less spacious and smaller than those in use in America and Germany, but newer British plants are fully in line with the best overseas practice. Greater attention will be paid to coal-blending in future British plants, though those erected at iron and steel works, drawing their coals from a variety of sources, are generally well equipped in this respect. The underjet method of oven heating appears to be generally accepted, and this is held to be the most significant advance in oven design in recent years.

Foreign practice is wholly in favour of self-sealing doors, but many clay-luted doors are used in British practice. Faulty design of self-sealing doors leads to deterioration of the ends of the ovens, and much thought is being given now to the evolution of a satisfactory design of self-sealing door. Much depends on keeping the doors cleaned and well serviced.

The pressures existing in the coke oven chamber under various conditions have been investigated by J. Hamilton and T. Kennaway.[20] This subject is to some extent bound up with the design of oven doors; a pressure is kept in the gas-collecting main to avoid any possibility of air-inleakage into the oven chamber, which would lead to carbon formation and other troubles, but if the pressure is too high, leakage at the oven doors may lead to discharge of smoke and gases which may fire and damage the doors and brickwork. There may be a difference in vertical height of some 20 ft. between oven sole and gas collecting main level, but superimposed on the buoyancy effect is that of the continuous generation of gas and the frictional resistance it must overcome in passing up the oven charge. The investigations made by these authors lead to the conclusions that it is possible to maintain the ovens under pressure at all times with 4 mm. water gauge pressure in the main except when charging and discharging, provided that the valves are manipulated on a schedule as required by the extent to which carbonization has proceeded; with 7–7·5 mm. pressure in the main it is not necessary to manipulate the valves but smokeless charging is then impossible and there is grave risk of damage to the structure due to leakage of gases.

The use of oil in coke ovens has been described by W. C. Wardner.[21] Reference is made in this paper to the now common practice of adding small quantities of oil to control the bulk density of the charge; in some plants a small and uniform quantity of oil is used to maintain consistent bulk density, while in others the quantity of oil used is varied to secure whatever bulk density is desired. Oil has also been used to increase the quantity of gas made from an existing coke oven battery; this is used in preference to the means adopted in Britain, the argument being that any effort to increase gas output by varying the oven conditions must affect the quality and quantity of the coke. In one plant Bunker 'C' oil was sprayed into empty ovens at 100 lb./sq. in. pressure and 150° F. through sprays placed in the charging hole lids, accompanied by sufficient steam to aid the cracking and to prevent excessive carbon deposition. Enrichment by natural gas of oven gas diluted with producer gas has also been used.

Gasworks practice

The high capital cost of coke oven plant has been referred to in the preceding section. There is equal ground for alarm in the gas industry from this cause, and it has been suggested that responsibility for the rise in cost lies not only in the general increase in the price of materials and labour but also in the more elaborate design now demanded, partly to provide amenities for the workmen that were not regarded as necessary ten years ago and partly to secure the elaborate architecture and general arrangements that have become customary in such buildings as gasworks'

retort houses. The suggestion has been made that these nationalized industries should give some thought to their minimum requirements with a view to helping designers to reduce capital costs.[22]

The problem of producing gas to meet peak loads economically has been discussed in a number of papers, particularly at the meeting of the International Gas Union in London.[23,24] Peak loads may occur at different hours during the day but are ironed out by the use of gasholders whereby the manufacturing plant can continue to operate throughout the 24 hours at as near to uniform load as is desired. Seasonal peak loads are generally due to the weather and cause the difficulty. F. M. Birks[24] has stated that in the London area some 35–40% of the gas made may be described as peak load, and as the temperature drops in winter, additional capacity must be brought into commission to produce the increased quantities of gas required. The load factor of plant to deal with demand at temperatures of 65° F. is of the order of 89%; at temperatures of 41° F. (the average London seasonal temperature for the three winter months of December, January and February) the load factor is only 15%, at 32 ° F. it falls to the negligible figure of 2%, with correspondingly high capital charges on the plant which is left idle for so much of its time. F. M. Birks considers that the temperature range 65° F. to 41° F. should be taken by the newest and most efficient plant for the base load and, as consumption mounts, there should be brought into use the older and less efficient plant to make gas for demands of shorter duration. When the plant has a high load factor, say in excess of 80%, it is considered justifiable to incorporate every possible refinement to secure a high degree of thermal efficiency. With plant intended to deal with demand covering lower load factors, and which must be shut down for periods every year, considerations of flexibility requiring simple and sturdy construction become of paramount importance. The increment of consumption occurring within a temperature range of 41° to 32° F. can best be met by carburetted water gas on account of the comparatively low capital costs of this plant. For the very occasional peak loads below 32° F. oil gas plant[25] is recommended. For London conditions the total gas-making capacity of the works might economically be made up of 50 to 65% of coal gas plant, 40 to 25% of C.W.G. plant and 10% of oil-gasification plant. France[23] seems to favour regulation by tariffs in order to encourage smoothing of the load. In both countries the opinion appears to be growing that the gas industry should not attempt to satisfy all the demands of the consumer by gas but that certain loads, particularly a great deal of the winter space-heating load, should be taken by solid smokeless fuels such as coke or low volatile coal. Tariff restriction on economic loads is now being introduced into U.S.A.; these rates put a severe economic penalty on purchases at 75% load factor, and are prohibitive at the load factors now developed in the domestic heating load.

Propane–air plant was originally introduced as standby equipment but is now used for meeting peak load demand.[26] In the Appalachian area of the U.S.A. there are from 10 to 20 days each winter when propane–air gas can be most economically used to cope with the demand peak. It is generally held that natural-gas companies cannot afford to make more than 2% of their annual sales in propane gas. Placed near the demand

area, propane–air plant eliminates the transportation problem and delivers gas at suitable pressure directly into the gas system with rapid starting up and shutting down as required and very low labour costs since the plants are operated electrically by push-button control; a 7 million cu. ft. a day plant can be operated with one man a shift. Outputs between 0·5 and 50 million cu. ft. a day can be provided by single plants. Methods used in U.S.A. described by R. D. Hendee[27] involve (i) adaptation of existing C.W.G. plants whereby their output can be increased by separating the oil-gas and water-gas operations, (ii) production of H_2 and CO from hydrocarbon oils, (iii) use of liquefield petroleum gas (e.g. propane), (iv) variation in calorific value by addition of natural gas to mains carrying manufactured gas, and (v) underground storage. A proposal has been made[23] to use in France abandoned coal mines for the storage of gas on a large scale in order to meet peak loads provided that the strata are sufficiently gas-tight. This appears at first sight to be an impracticable proposal but in America over 200,000 million cu. ft. of natural gas are now stored underground largely in the Appalachian region in abandoned or partially depleted natural-gas wells; these are repressured during off-peak periods and drawn on during peaks, but apparently are used wholly on natural gas at present.[27,28]

Another gas storage problem which has been discussed during this year is that created by the provision of gas for industrial loads required by factories operating a five-day week and involving the cessation of manufacture at the week-end. This is a very common difficulty in industrial areas in Britain but is international. Its effect on the Ruhr Gas Grid has been described by H. D. Greenwood and W. R. Branson.[29] These authors point out that the cost of gasholder storage depends on the use made of the storage. They state that low-pressure gasholders, in sizes of 100,000 cu.m. and upwards cost 7·5–5·5 RM a cu.m. at pre-war German prices. If a mean figure of 6·5 RM be taken and capital charges, depreciation and maintenance at 15%, the cost per cu.m. of gas stored is as given in the following figures:

Number of fillings per annum	Cost in Reich-pfennig per cu.m. stored
25	3·9
50	1·95
100	0·975
150	0·65
250	0·39

The use of propane or other liquefied gases for meeting peak loads may become of interest in this country in view of the large number of petroleum refineries now under construction or to be built within the next few years.[30] Attention has been focused during the year on the possibility of using the cracked gases from these petroleum refineries for town gas purposes. The technical arrangements that have been made to supply large quantities of petroleum gas from the plant of Manchester Oil Refineries Ltd. to Manchester Corporation Gas Department (now the Manchester Division of the North-Western Gas Board) have been described in considerable detail.[31,32] It was expected that there would be available from this plant

600,000 cu. ft. a day of 890 B.Th.U./cu. ft. A similar link-up between the Ellesemere Port Plant of Lobitos Oilfields Ltd. and Ellesmere Port Gas Undertaking[33] has proved equally satisfactory, and since the inception of the scheme in March 1949 the amount supplied has averaged 60,000 cu. ft. a day of gas of 1500 B.Th.U./cu. ft. This gas is mixed with manufactured gas of C.V. 340 B.Th.U./cu. ft. to give a final gas of 430 B.Th.U./ cu. ft. for distribution. The use of the increasing quantities of refinery gases which will be made available has been discussed during the year under review[34]; the suggestion has been made that this is a matter which should be taken up by the Ministry of Fuel and Power and by the two industries concerned in order to discover the economic price at which it will pay refineries to use solid fuel or heavy oil fuel for internal heating purposes and to release the maximum quantity of refinery gases to the gas industry. It has been suggested[34] that when the full refinery programme has been built the amount of gas available might be as much as one-quarter of the total thermal value of the manufactured gas now distributed in the country.

The use of methane synthesis as a method of enriching carburetted water gas, to which reference will be made later, comes within this general category of new methods of enriching blue water gas or other gases made from total gasification processes. It is of interest to observe that a proposal has been revived by E. Crowther, speaking at a meeting of the Institution of Gas Engineers, to distribute gas of the order of 360–400 B.Th.U./cu. ft. made direct from gasifying in steam the residual coke after carbonization and adding the resulting B.W.G. to the coal gas made in the retorts, thus avoiding the need for enrichment.

One result of nationalization will be to secure a greater degree of uniformity in the calorific value of town gas, not perhaps over the whole country but at least over the territory of each Area Board. The declared C.V. must enable the C.V. and specific gravity to be controllable within close limits, the combustion characteristics to be constant and satisfactory for the appliances in use, the C.V. must be high enough to enable the existing mains to carry the gas without overloading and the cost per therm delivered to the consumer must be as low as possible. The quality of the coal is a governing factor since the more mature coking coals generally yield the richest gas. There does not appear to have been any move yet in the direction of standardization of calorific values in this country. The subject was discussed by the Association Technique de l'Industrie du Gaz en France[35] at the meeting of the International Gas Union and the conclusion was reached that for France the optimum C.V. was between 420 and 500 B.Th.U./cu ft. though special conditions might lead to the use of a gas above or below these limits. In France the established limits are 366 to 471 B.Th.U./cu. ft. although consumers' appliances can take C.V. between 314 and 525 B.Th.U. The majority of gas undertakings in Great Britain distribute a gas of declared C.V. between 450 and 500 B.Th.U.

An important paper published during the year on plant design was a review by J. Burns and F. R. Weston[36] on the effect of changes in the taper in continuous vertical rectangular retorts built for the Gas Light & Coke Company of London between 1912 and the present date. The earlier

retorts, 1912–23, had some taper at the upper portion of both the major and minor axis, the lower portion being straight-sided. Between 1929 and 1944 there was no major axis taper in new retorts but the top portion of the minor axis was still tapered. In all of these retorts there was difficulty in securing uniform travel of the charge. Between 1944 and 1948 retorts were built with no taper on the major axis but a continuous taper on the minor axis from top to bottom of the retort. The travel of the charge in these retorts is claimed to have been more uniform and the carbonizing results improved, particularly on Durham coals which tend to exert fairly considerable or high swelling pressure in the plastic range. A further bench of retorts is to be built with continuous taper on both major and minor axis in order to determine whether further improvement results. It would seem that there is some difficulty in effectively decomposing steam at the bottom of retorts having continuous taper from top to bottom, and this may indicate that the minor axis should not be continued right to the bottom.

A comprehensive paper to the International Gas Union by Association Technique de l'Industrie du Gaz en France[37] discussed the factors which should be taken into account when choosing a type of retort for any particular set of conditions. This report studied layout, dimensions, fuel for heating, labour, flexibility, working life, and so forth, and set out the conclusions in a comprehensive diagram giving the type of plant suitable for consideration for works having a daily production between 125,000 and over 7 million cu. ft. together with an indication of the recommended systems for heating and dilution of gas (i.e. steaming, producer gas, water gas). The shortage of gas-making plant is reflected in the attention which has been paid since the war to methods of increasing the gas output from existing plant without any considerable expenditure in new equipment. The gasification of oil[38] has generally been discontinued in view of its high price. W. S. Hubbard[39] has described the methods used to increase gas output at Liverpool. Charging machines on horizontal retorts were replaced to permit of the retorts being filled to their maximum capacity. Mechanical producer plants were installed[40] at the two larger stations where water gas plants were also in existence so that, in emergency, rich gas up to 600 C.V. could be made on the C.W.G. plant for dilution by producer gas, thus permitting the addition of up to 10 million cu. ft. of producer gas a day. Modifications in procedure were made which enabled the output of an installation of Woodall-Duckham continuous vertical retorts to be increased from 5·9 to 6·9 million cu. ft. a day of gas of C.V. 450 B.Th.U./cu. ft. The continuous vertical retort plant was operated so as (i) to put the maximum quantity of coal through each retort consistent with reasonably low loss of volatile therms in the coke (ii) to make the highest C.V. gas by reducing the steam admitted to the retort to an amount sufficient only to utilize the sensible heat of the coke for the water gas reaction and to avoid over-heating of the bottom casting or seating joists. The C.V. of gas at inlet to holders was then controlled by admission of producer gas as a diluent added at the inlet to exhausters. In addition to the increase in the daily output of the works by 25% and a saving in the amount of steam admitted to the retorts by 20%, the fuel consumption was reduced from 10 lb. dry coke

per 100 lb. wet coal to 9·5 lb. with the same maximum combustion chamber temperature of 1380° c.

There is an increasing belief in some quarters that the fuel industries should not be considered as separate entities but that their technical practice and processes should be combined. If this idea proves to be acceptable it will now be easier to put into effect by reason of nationalization: this would render it comparatively simple to combine operations now conducted separately by the National Coal Board (Carbonization Branch), the Area Gas Boards, and the British Electricity Authority. R. Schriber[41] has maintained that the optimum method of energy supply lies in the utilization of the available water power sources with the minimum coal consumption to produce a maximum output in the form of electricity and heat. In order to fulfil this there are five basic requirements: (i) High efficiency in the generation of energy (ii) utilization of all installations to the maximum capacity (iii) peak demands to be adequately covered (iv) the consumer to be supplied under safe and reliable conditions with energy in a suitable form and (v) low price of energy. The practical side of this proposal appears to be a combination of heat-power station with water reservoirs for the production of water power whenever sufficient water is available, and with a gasworks to provide solid fuel for the power station and gas for sale. The coke produced in the summer would be stored against winter demands for use when water power was not available in sufficient quantities. Clearly this is a method dependent on there being adequate water power available. A more practical method of combining the gas and electricity industries has been devised by F. Stief of Hamburg Gasworks[42] in which the (non-coking) coal now supplied to the power station boilers is to be carbonized in inclined chamber ovens at Hamburg Gasworks at medium temperatures. After carbonization the coke is screened, and the larger sizes are used on travelling grate stokers or in forded draught furnaces; the dust is carbonized as pulverized fuel in the boilers, or the whole of the coke can be crushed for pulverized fuel firing. The combined works thus sets out to make gas, the usual by-products, and electricity; it could also produce hot water for district heating purposes.

Coke

The Ministry of Fuel and Power's 'working group' has reported on the use of the sensible heat of hot coke discharged from gasworks and coke ovens in this country.[43,44] Existing plants will give adequate performance if properly maintained. Applied to static carbonization in gasworks the process is reported as not showing any outstanding economic advantage. In continuous vertical retorts the sensible heat of the coke is already largely recovered by other means. At coke oven plants where a steam yield may be expected of approximately 1000 lb./ton of coke cooled the economic return is sufficient to warrant careful consideration. L. H. W. Savage and A. V. Brancker[45] have described the systems of dry coke-cooling available and their application to an integrated iron and steel works and have concluded that the application of dry coke-cooling in these works depends primarily on the running costs of the process, the ability to use the steam raised and to use the fuel that would otherwise

have been required to raise the steam ; in general, their conclusions were not altogether favourable to the adoption of the process on steelworks. F. Pearson[46,47] disagrees fundamentally with these conclusions, arguing that outstanding economies in fuel that have been made in blast furnace practice at Ford's works at Dagenham are attributable in a major sense to the use of dry-cooled coke, and that the dry-cooled breeze, being readily screenable, can be put to uses which make it as valuable as large coke. G. E. Foxwell[44] has summarized the various arguments and has concluded that a good deal of the attractiveness of dry coke-cooling, apart from the small-to-moderate profits shown by the Ministry's working group, is attributable to indirect savings such as those claimed by Pearson, and to such advantages as the improvement in quality of the coke and reduction of corrosion on the works, arising from wet quenching sulphurous steam. The need for some form of alternative cooling plant as standby is evident. Until these aspects of the subject have been thoroughly investigated it is unlikely that many dry coke-cooling plants will be built in this country unless the price of coal increases still further ; in Switzerland where the price of coal is understood to be of the order of £10 a ton, nearly all the gas works operate dry coke-cooling plants.

The quality of open grate coke has again been under discussion.[48] John Roberts[49] has discussed previous work and has described the large-scale experiments on blending coking and non-coking coal carried out by the Severn Valley Gas Corporation and others during recent years. In the change-over from private enterprise to nationalized administration, the need for providing for large towns greater quantities of solid smokeless fuel and appliances in which to burn it appears to be neglected, and the Simon Report that focused attention upon it, to have been pigeon-holed. Increased emphasis has been laid during the year upon total gasification and the control of the coke market by internal use of whatever coke is produced : this would seem to be a mistake in policy if only because of the known difficulties of producing peak load gas at an economic price.

The British Iron and Steel Research Association and the British Coke Research Association have jointly considered a statement of coke quality for blast furnaces which is not a specification or an accepted measure of quality but an indication of the present views of the iron and steel industry.[8] According to this statement blast furnace coke should not be below 1 in. in size with a tolerance of 5% in quantity below this size ; the moisture content should be constant and not above 3% ; the ash content should not vary by more than $\pm$ 1% with an average ash content not higher than 10% ; the sulphur content should be as low as possible ; and the coke should show at least 85% on the 1½-in. shatter test with not less than 97% on the ½-in. shatter test. T. Sanderson[50] has also discussed this subject and has given the reasons for the foregoing conclusions. R. P. Towndrow[51] has discussed fuel efficiency in blast furnaces and the utilization of blast furnace and coke oven gas. He has confirmed the deleterious effect of coke fines below 1 in. in size and of the need for the coke to be sufficiently strong to withstand the severe impact and abrasion loads imposed upon it, while being resistant to oxidation by CO_2 and yet sufficiently reactive to burn rapidly upon reaching the tuyères. Given the proper physical characteristics the value of a coke depends upon

its carbon content. Great attention should be paid to the preparation and blending of coal for the production of metallurgical coke, starting with careful preparation and washing of the coal, blending, fine crushing to reduce the size of the shale particles and scientific control of the carbonizing process.

An interesting study of the sources of sulphur in coke has been made by S. E. Eaton, R. W. Hyde and B. S. Old[52] using radioactive tracers. It is generally recognized that sulphur exists in coke as pyritic, organic and sulphate sulphur. Since the sulphate sulphur of most coals is very small, the experiment was designed to indicate how much organic and pyritic sulphur remains in the coke after carbonization. The result indicated that pyritic and organic sulphur appear in the coke in proportion to their concentration in the coal.

More coke breeze is used for steam raising purposes at gasworks. The Oldbury stoker used for this purpose has been previously described,[53] and this year a further description has been given of a breeze-burning plant at Ascot gasworks giving a boiler efficiency of 68% from coke breeze almost wholly below $\frac{1}{2}$ in. in size.[54] The most important paper this year on coke utilization is a description of an entirely new development, the 'down-jet furnace,' emanating from the British Coal Utilization Research Association Laboratories.[55] Coke is fed by gravity from a closed hopper to form a bed inclined at the angle of repose. A jet of air, which can be preheated, is blown on to the upper surface of this bed at a velocity of 100–200 ft./sec. Combustion takes place in a layer just beneath the surface with generation of intense heat and production of an outlet gas containing in normal industrial practice 18 to 19% CO_2. The ash fuses and the molten drops fall to the bottom of the bed where they coalesce and solidify to form an easily removable clinker. The principle has been applied to boilers and furnaces operating both at low and high temperatures.

Gas purification

In the first step in purification, namely cooling with condensation of water vapour, the recovery of the sensible heat of the gases has been attempted in the past but is difficult in practice by reason of deposition of tar; recovery of heat from the water used in the primary condensers is more promising.[56] The practice of spraying with water the hot gases in the collecting main or in the Congdon pipes is becoming general; this replaces their sensible heat by the latent heat of water which must again be removed in the condensers where the real work is done. Such published results as are available do not appear to be in line with theoretical considerations and it is suggested that investigations should be conducted to correlate the results on gas-cooling equipment with fundamental work on heat transfer. The selection of an indirect water-tube gas cooler has been discussed by K. W. Francombe and A. G. Grant.[57] The volume, temperature and saturation temperature of the gas should be specified at the point of entry to the condenser, and also the required gas outlet temperature and the temperature of the cooling water in summer and winter. Condensers cannot be compared on a basis of 'price per unit cooling surface' since the effectiveness of the cooling surfaces may vary

considerably according to the gas and water velocities employed. In selection, capital charges must be balanced against water costs—the larger the condenser the smaller the quantity of water that must be used—and the pressure drop across the condenser is related to the power costs of the exhauster. The pressure loss across a condenser varies as (gas velocity)^2 and heat transfer varies as (gas velocity)$^{0.75}$, hence if the gas velocity is doubled the heat transfer coefficient is increased to 170% and the pressure loss to 400% of the original figure. The high-velocity vertical-tube condenser has largely superseded the horizontal tube type owing to ease of cleaning, avoidance of corrosion due to air trapping, and ease of construction. Gas velocities of 3–6 ft./sec. (at S.T.P.) are used in horizontal-tube condensers and 6–12 ft./sec. in the vertical tube type.

The electrostatic detarrer has now become an integral part of all gas purification or by-product recovery plants. The first comprehensive paper on the application of electrostatic precipitation to coal carbonization was given by K. W. Francombe.[58] The efficiency of tar fog extraction depends on the dimensions of the extractor, the gas velocity, composition and temperature and on the potential and wave form of the direct current applied to the discharge electrodes. The main discharge should be of the corona type 20–33 kv. with as little sparking as possible. The collecting electrodes are usually 9–12 ft. long; gas velocities 3–5 ft./sec. in tubular collecting electrodes (6-in. diam.) and half this in plate electrodes. The total cost of operation is of the order of 0·0025 pence/1000 cu. ft. of gas. Detarrers are usually designed to give 99% extraction and to obtain the highest removal of tar should follow the exhauster. The detarrer introduces into the gas stream a source that would ignite any explosive mixture that may be present; the Safety Rules Committee of the Institution of Gas Engineers has issued a code of practice for the safe operation of electrostatic detarrers on gas works.[59]

The economics of gas washing in static (bay) washers have been discussed at C. Cooper[60] with reference to ammonia, benzole and naphthalene. The overall cost of washing ammonia from the gas is considered as made up of capital and maintenance charges (at 10%), power (at 1d./kwh.), water (at 1s./1000 gal.) and distillation or handling cost (this varying from nil when sent to a distiller who pays only cost of transport to 10s./ton, representing carriage over 30–40 miles). The conclusion is reached that cost of disposal largely governs the quantity of water used and therefore the most economical size of washer. The larger the washing surface the smaller is the permissible quantity of water to be used in any given circumstances. It is good practice to use more washing liquor and smaller washers when the cost of disposal is anything but the most expensive, and to cut down the number of bays in use to economize in power. In washing benzole from the gas where steam and oil costs and the degree of recovery must be taken into consideration, it is concluded, on the other hand, that the advantage lies on the side of using more units in the washer. In benzole recovery and in naphthalene removal, the cost of the steam is the dominating item, so that the oil rate should be kept low and the equipment increased to make the low rate effective.

The removal of hydrogen sulphide from gas has continued to be the

subject of discussion and experimental work, resulting in important conclusions. Plants operating the Manchester wet purification process[61] are under construction at three or four gasworks and coke oven installations; the working results are awaited with interest. J. J. Priestley[62] has discussed the basic principles of liquid purification. Opinion is divided as to whether the liquid purification process should aim at complete removal of H_2S to Gas Referees' standard or at partial removal to reduce the load on the purifiers; the ultimate objective is mechanization of an operation which now entails much manual labour. Virtually all known processes of liquid purification can be classified into three groups: (i) absorption of H_2S in a solvent followed by desorption (ii) absorption and oxidation of H_2S to S or thiosulphate or both (iii) absorption and fixation of the absorbed H_2S with SO_2 and NH_3.

While efforts are being made in many countries to evolve suitable liquid purification processes that remove H_2S effectively without producing difficult and voluminous effluents, the Gas Research Board and the laboratories of the North Thames Gas Board are working on the improvement and ultimate mechanization of the oxide process. L. A. Moignard[63] has summarized earlier work[64] and attention must be directed here to a still earlier publication by G. U. Hopton and R. H. Griffith[65] describing the characteristics and reactions of the seven known forms of ferric oxide, work which is leading to the production of iron oxide in a far more active condition than the material used at present for gas purification. Investigations by the Gas Research Board into the subject of the hardening of oxide in purifiers[66] have confirmed an observation made by H. B. Avery in 1939[67] that when iron oxide is alternately sulphided and revivified its structure can be completely disrupted in such a manner that the sulphur accumulates inside the particles, the iron migrating outwards so as to remain on the surface. This reaction requires the presence of moisture, and the migration appears to be due to the solution of iron sulphide in the moisture film in the presence of CO_2, after which the sulphide is reoxidized at the surface of the film with deposition of the iron in active form as the γ-ferric monohydrate.[68] The first stage in oxide purification is the absorption of H_2S with formation of ferric sulphide and the migration of the ferric sulphide to the surface where it is reoxidized (as just stated) so that the iron remains accessible to hydrogen sulphide. If migration ceases the surface layers become embedded in sulphur; the black colour of caked oxides can be attributed to unoxidized sulphide, and the glossy appearance and loss of activity of material to the surface sulphur film. The final stage of hardening is slow recrystallization of the superficial film of sulphide. In order to prevent hardening it is necessary to ensure that conditions are not set up which cause migration to cease; such conditions are (i) drying of the oxide (ii) too vigorous superficial reaction with the revivification air, and (iii) exposure to too high a temperature with the formation of unoxidizable sulphide. It is believed that the essential precaution is to keep a film of moisture on the oxide during practically the whole time it is in use.

Another attempt to mechanize the oxide purification process is the application of the fluidization technique. R. H. Williamson and J. E. Garside[69] have continued the work referred to in last year's ANNUAL

REPORTS[70] with promising results though these have not yet been taken beyond the laboratory stage.

The recovery of sulphur in elementary form from spent oxide has become an objective in the gas industry. F. J. Dent and L. A. Moignard[66] have described preliminary work using for extraction purposes a hot solvent (e.g. toluene) from which the sulphur will crystallize on cooling. It appears that every care must be taken to remove tarry matter before the oxide absorption boxes. The extracted oxide appears to be more active than that of the original oxide before use. The only further development that appears to have been published this year on the removal of organic sulphur compounds from town gas is that the Gas Research Board has a promising process on the laboratory scale which operates on the hot crude gas, leaving an electrostatic tar extractor operating on the foul main. The gases pass successively over two catalysts: (i) molybdenum sulphide on activated alumina, and (ii) copper–chromium on active carbon. The process is working satisfactorily over long periods on a small scale but it remains to discover a method of regeneration of the catalysts to reduce its cost. German work on the desulphurization of residual hot gases containing benzene has been reported.[71] An alkali hydroxide catalyst was used at temperatures ranging from 50° to 400° c. and 6–8 atm. pressure. The organic sulphur content of the coke-oven gas of 40–50 g./100 m.^{3} was reduced to 4·3 g./100 m.^{3} (89·5%) at 200° c. and to 2 g./100 m.^{3} (95·1%) at 400° c. The sulphur content of the benzene was reduced from 1 g. to 0·22 g./100 cm.^{3} (80%). The gas composition changed slightly: the carbon dioxide content increased and the hydrogen content decreased. The increase in benzene content average 17%.

A description has been published[72] of what is believed to be the oldest working gas holder in the world, built probably in 1827, at the Fulham Works of the North Thames Gas Board. The use in U.S.A. of gas distribution and service pipes made of plastic material has been described by S. A. Bradfield.[73]

Ammonia

Ammonia in carbonization practice remains a problem since it is rarely that ammonium sulphate plants can be operated at a profit. Efforts are being made by the British Sulphate of Ammonia Federation to reduce the cost of production primarily by reducing steam requirements and maintenance.[74] P. J. Wilson and J. H. Wells[75] consider that the principal opportunities of lowering the cost of recovering ammonia are (i) substitution of a cheaper material than sulphuric acid for fixing ammonia (ii) manufacture of concentrated liquor (iii) recovery of H_2S in a form suitable for the manufacture of sulphuric acid and (iv) manufacture of salts other than sulphate. These possibilities are considered in detail but the authors' conclusion is that in U.S.A. manufacture of ammonium sulphate is still the best method for disposing of ammonia and that the semi-direct process has not yet been seriously challenged. W. Reerink[76] has suggested the use of humic acid as an alternative to sulphuric acid and claims that field trials in Westphalia by the Agricultural Advisory Bureau have shown better yields from land treated with 'ammonium

humate' than with ammonium sulphate. The present production cost of by-product ammonia is stated to be 50% higher than the income; in his view the most promising method of reducing costs is to discover a means of using the hydrogen sulphide in the gas for the manufacture of sulphuric acid. H. Bruckner[77] claims that extensive experiments have shown that ammonia liquor and artificial humus fertilizers based on ammonia are equivalent to those of the more usual forms of commercial ammonia fertilizer.

Recovery of thiocyanates from ammonia liquor may become attractive because of the demand for them for the production of amino-plastics. Ammonia wash liquor usually contains from 0·2 to 0·3% ammonium thiocyanate and the liquid which condenses in the oxide boxes may contain from 20 to 30% of this salt together with from 2·5 to 3% iron thiocyanate. Where lime is used for purifying the gas the calcium salt is leached out. One American patent protects a system of successive scrubbing in scrubbers which must all contain sulphur and, by a system of recycling, permits a strong ammonium thiocyanate solution to be drawn off from time to time. Several other patents cover methods of substituting magnesium compounds to treat gas which has been freed from tar and ammonia, or for more direct application.[78] The recovery of pyridine from ammonia plants has been suggested by S. A. Ashmore and D. Thickins.[79] Saturator liquor from semi-direct plants was found to contain between 0·4 and 7·7% of pyridine bases, and substantial amounts of these compounds were also found in the gas leaving the saturator. It is pointed out that the usual test for slip of ammonia in the gas leaving the saturator does not give a true estimate of ammonia but of alkalinity due to pyridine bases and ammonia.

The disposal of effluent liquor from carbonization works, most of which is derived from the recovery of ammonia, has become a major problem in the carbonization industries. A description has been given by G. E. Currier of an elaborate plant at the new gas works under construction at Tingley[80] designed to convert the ammonia liquor into an effluent sufficiently pure for direct discharge into streams. Comprehensive surveys of the practical and chemical aspect of ammonia liquor disposal have been published.[81,82]

Other by-products

The recovery of ethylene from coke oven gas by liquefaction has been described by P. M. Schufton and J. Neill.[83] These authors conclude that it has now become possible for the first time economically to produce ethylene as a main product from coal and at a price commercially competitive with that of production of ethylene from oil cracking.

Theoretically, the most exciting possibilities in gasification depend on the use of oxygen. If medium-purity oxygen could be manufactured at a limited cost the direct high-pressure hydrogenation method of total gasification of coal or semi-coke could be put into industrial operation to make gas of 500 B.Th.U. quality, continuous processes making gas of some 300 B.Th.U. would be feasible and many of the processes used in the iron and steel industry could be conducted with a much higher thermal efficiency. In many quarters there is a belief that low-cost oxygen has

already been achieved. J. R. Park[84] has summarized the position thus: 'There has been a great revival of interest, some very fresh thinking, and a concentration of chemical engineering effort on the problem of separating air; but from the economy point of view there has been no really major change during or since the war.' All processes are variations of the Linde and Frankl process and, like it, are dominated by low thermodynamic efficiency and high power costs. The general plan involves a refrigerator in which work done on the air is converted into cold, a heat exchanger to reduce heat losses, and purification and rectification systems. On such a cycle power consumption is of the order of 0·7 kwh./cu.m. and thermodynamic efficiency 13% for oxygen gas of 90–98% purity. If a lower purity is permissible the power consumption can be reduced to 0·5 kwh. by using a low-pressure regenerator plant with an efficiency between 16 and 19%; this type of plant (J. R. Park, *loc. cit.*) is not normally an economic proposition below 23,000 to 30,000 cu. ft./hr. (22–30 tons/day); continuity of production and large consumption are necessary for the cost of production to be reasonably low. The major stumbling block to substantial reductions in cost is the difficulty of raising the efficiency of the compressors.

Under German conditions, according to E. Karwat,[85] oxygen of 73% purity can be produced at the rate of 16,500 cu.m./hr. at the following costs, using (*a*) blast furnace gas turbine and (*b*) steam engine as prime mover:

	(*a*) RM on 1938 price basis	(*b*) RM on 1938 price basis
Capital charges	600,000	555,000
Power and cooling water	325,000*	579,000†
Secondary materials	10,000	10,000
Wages	156,000	144,000
	1,091,000	1,288,000
Cost per cu.m. O_2	0·76	0·9

* Prime mover .. blast furnace gas turbine
† ,, .. steam

Particulars published of other plants indicate claims for a lower power consumption than that suggested by Park. J. Wuckerer[86] gives figures for five processes all between the limits of 0·416 and 0·495 kwh./cu.m. of 95% O_2; J. Grunberg[87] claims for the 'oxyton' process 0·405 kwh./cu.m. of 95% O_2 when treating 20,000 cu.m. of air an hour in each case. No recent figure appears to have been published of the permissible cost of oxygen for gasification purposes, and it is difficult to pronounce with certainty on this subject since other costs involved in the processes of gas manufacture cannot be known until a plant has been erected and operated on the manufacturing scale.

Producer gas

J. R. Arthur has published a comprehensive survey of recent researches on the combustion and gasification of beds of solid fuels.[88] He concludes that one of the striking results of recent work is to show that the combustion and gasification of solid fuels proceed by a series of formally

elementary reactions in which simple species (atoms and radicals) play the dominant role. In the exothermic reactions, a very great responsibility rests with the chain carriers such as H, H_2 and H_2O which lead to fully-burnt gases. If technological advances are to be made in improving existing practice in this field, the detailed chemical kinetics must be taken into account. Having established what are the elementary contributing reactions, it remains to ascertain how they may be affected by, and if possible, controlled in, the complicated topochemical environment which exists in technical fuel beds. Recent developments in gas producers, particularly in regard to the effects of segregation and the avoidance of segregation, have been summarized.[89] Mechanical producers are becoming increasingly used for heating gas retorts and two papers on this subject are deserving of study.[90,91]

Water gas

C. E. Utermohle[92] relates that in view of the U.S. Gas Industry's interest in high-C.V. oil-gas the producton research committee of the American Gas Association has sponsored a series of tests using cheaper and heavier hydrocarbon oil on an existing twin generator set. The hourly capacity when using a high-carbon oil is approximately 70% of that with a low-carbon gas oil. Operation was found to be satisfactory and a considerable saving in fuel cost would result because of the price difference between the two types of oil. Another attempt to make C.W.G. from heavy oils has been recorded by E. L. Hall[93] in a plant consisting basically of the carburettors and superheaters of two adjacent water-gas generators, not used themselves, and with a large cross-over connexion installed between the tops of the carburettors. An increased thermal capacity of 35% with a fuel saving of 30% (thermal efficiency 79%) is claimed, together with continuous production of gas having a C.V. of 1000 B.Th.U./cu. ft.

Work on the catalytic production of methane by the reaction: $CO + 3H_2 = CH + H_2O$, has been continued by the Gas Research Board, on a pilot plant scale.[94,95] This process uses high-temperature coke as the starting point, whereas the pressure hydrogenation process mentioned previously under 'Gasification—Town Gas' requires coal or semi-coke; the processes are thus complementary. F. J. Dent and D. Hebden[95] have described the methods used for overcoming operational difficulties. Deposition of carbon on the catalyst and sintering of the catalyst can be prevented by 'catalyst dilution,' e.g. by reducing the ratio of nickel to promotor (in which it is dispersed) from 10 : 1 to 1 : 2, and by preventing the catalyst from rising above 500° c. when working at atmospheric pressure and above 600° c. at 25 atm. by circulating synthesis gas containing (volumetrically) H_2 : CO less than 2 : 1. The heat of reaction is removed by circulating the hot gases through a waste heat boiler before re-circulating them through the catalyst. Complete purification of the synthesis gas to less than 0·002 grain of S/100 cu. ft. still requires investigation in its application to large-scale work. It is considered that the methane synthesis plant could now be transferred to the works scale as a method of enrichment of B.W.G., replacing oil when making base load gas. The thermal output of the generator is reduced, so that oil must be used when dealing with peak demands. The economics of the proposal

can only be established by large-scale operation. A second method in which the methane synthesis could be used is considered to be the gasification of coke breeze in oxygen-blast generators at 10 atm. pressure, some or all of the resulting gas being subjected to synthesis; this method awaits cheap oxygen as previously indicated before it can be used in manufacturing practice.

Underground gasification

The Ministry of Fuel and Power is to undertake an experiment on underground gasification at the open-cast workings at Newton Spinney, Chesterfield.[96] Here there is an outcrop of the Fox Earth seam, which contains 18 in. of good coal. In the face which is exposed beneath some 40 ft. of overburden, a 4-in. borehole is to be drilled some 250 ft. into the seam. It will be connected by two vertical boreholes 50 ft. apart, extending to the surface, the extreme point being about 80 ft. below the surface. This is purely a pilot-plant scale experiment, and it is understood that a gas of not much above 50 B.Th.U./cu. ft. is expected to be produced. The objective is to find means for the recovery in this way of coal unworkable by normal methods.

American experiments have proceeded farther, and a second series of trials is projected at Alabama, U.S.A.[97] The objectives are stated to be the production of synthesis gas for oil manufacture, cheap fuel gas for power production, and economic utilization of thin seams uneconomical to mine; a 42-in. seam is being used for these experiments. Air-blow is intended to set up a temperature of 1650° C. from which hot combustion products will distil the coal and form CO. The remaining coke is expected to act as fuel for the fire as it works its way along. Work is proceeding in Belgium and Russia, and probably in other countries.

References

1 ANNUAL REPORTS, 1947, **32**, 25; 1948, **33**, 37
2 Gas Act, 1948
3 *Coke and Gas*, 1949, 187
4 *Gas J.*, 260, 520
5 *J. Inst. Fuel*, 1948, **21**, 279
6 *Coke and Gas*, 1949, 195
7 Thomas Hawksley Lecture, Inst. mech. Engrs., 1949
8 Cf. D. Hicks and G. W. Lee, U.N. Sci. Conf., 1949; *Coke and Gas*, 1949, 361
9 *Fuel*, **28**, 97
10 *Glückauf*, **81–84**, 452
11 Wm. Young Memorial Lecture, *Gas World*, **130**, 1605
12 Fuel Research Technical Paper No. 29
13 ANNUAL REPORTS, 1948, **33**, 44
14 *Gas-u. Wasse. fach.*, **90**, 149
15 *Chem. Engng. News*, **27**, 1500
16 *Coke and Gas*, 1949, 233
17 *Gas World* (*Coking Section*), 1949, 19
18 Private communication
19 *Blast Furn.*, **37**, 427
20 *Gas World* (*Coking Section*), 1949, 47
21 *Amer. Gas Ass. Mon.*, **30**, 30
22 *Coke and Gas*, 1949, 169
23 Int. Gas Union, Paper 4, "Report of the Association Technique de l'Industrie du Gaz en France"

[24] Birks, F. M., Int. Gas Union, Paper 12, "The characteristics of a gas-making plant to meet the seasonal heating load"
[25] *See* ANNUAL REPORTS, 1948, **33**, 49
[26] Lauderbaugh, A. B., *Amer. Gas Ass. Mon.*, **31**, 12
[27] *Inst. Gas Engrs., Comm.* 350
[28] Fruechtenicht, H.L. and Simpson, J. B., *Amer. Gas Ass. Mon.*, **31**, 18
[29] Int. Gas Union, Paper 14, "Present and Future Problems in Coke Oven Gas Supply in Western Germany"
[30] ANNUAL REPORTS, 1948, **33**, 51
[31] *Coke and Gas*, 1948, 41
[32] *Gas World*, **130**, 1823
[33] *Coke and Gas*, 1949, 424
[34] Ibid., 149, 169
[35] Int. Gas Union, Paper 2, "Determination of the optimum C.V."
[36] *Inst. Gas Engrs., Comm.* 359
[37] Int. Gas Union, Paper 3, "Choosing a type of retort"
[38] *See* ANNUAL REPORTS, 1947, **32**, 33.
[39] *Gas World*, **130**, 60
[40] *See* ANNUAL REPORTS, 1948, **33**, 47
[41] *Gas-u. Wasserfach*, **90**, 383
[42] *Coke and Gas*, 1949, 384
[43] Report of Working Group of the Ministry of Fuel and Power; *Gas World*, **130**, 1257, 1302; cf. ANNUAL REPORTS, 1947, **32**, 30
[44] *J. Inst. Fuel*, **22**, 393
[45] *J. Iron Steel Inst.*, **161**, 103
[46] *Gas World*, Coking Section, 1947, 7
[47] *J. Inst. Fuel*, in press
[48] cf. ANNUAL REPORTS, 1948, **33**, 50
[49] *Coke and Gas*, 1949, 173
[50] *Gas World*, Coking Section, 1949, 119
[51] *J. Inst. Fuel*, **22**, 222
[52] *Amer. Inst. min. metall. Engrs.*; *Met. Technol.*, **15**, Tech. Pub. 2453
[53] ANNUAL REPORTS, 1948, **33**, 50
[54] *Coke and Gas*, 1949, 299
[55] Ross, F. F. and Sharpe, G. C. H., *Coke and Gas*, 1949, 389
[56] *Coke and Gas*, 1949, 315
[57] *Gas World*, **130**, 817
[58] *Inst. Gas Engrs., Comm.* 358
[59] Ibid., *Comm.* 355
[60] *Gas J.*, **257**, 645
[61] *See* ANNUAL REPORTS, 1947, **32**, 35; 1948, **33**, 53
[62] *Gas World*, **130**, 262
[63] Ibid., 860
[64] *See also* ANNUAL REPORTS, 1948, **33**, 52
[65] *Inst. Gas Engrs., Comm.* 288
[66] Dent, F. J. and Moignard, L. A., Gas Research Boad, *Comm.* GRB 52
[67] *Chem. & Ind.*, 1939, 171
[68] Griffith, R. H. and Plant, J. H. G., private communication
[69] *Inst. Gas Eng., Comm.* 357
[70] ANNUAL REPORTS, **33**, 52
[71] Board of Trade, German Div. Doc. Unit, F.D.X.244, Frames 596–609, 873–877
[72] *Coke and Gas*, 1949, 244.
[73] Ibid., 281
[74] Bell, J., *Gas World*, Coking Section, 1949, 105
[75] Wilson, P. J. and Wells, J. H., *Blast Furn. Plant*, **36**, 806, 961
[76] *Coke and Gas*, 1949, 411
[77] *Gas-u. Wasserfach*, **90**, 378
[78] *Chem. Age*, **60**, 481
[79] *Coke and Gas*, 1949, 307
[80] *Gas World*, **130**, 1708
[81] *Coke and Gas*, 1949, 240
[82] Badger, E. H. M., *Inst. Gas Engrs., Comm.* 360

[83] *Coke and Gas*, 1949, 27
[84] *Iron Coal Tr. Rev.*, **158**, 901
[85] *Stahl u. Eisen*, Dec. 2, 1948; *Iron Coal Tr. Rev.*, **158**, 577
[86] *Iron Coal Tr. Rev.*, **159**, 723
[87] Ibid., 1239; Lecture to the Physical Society
[88] *B.C.U.R.A. Mon. Bull.*, 1949 (Sept.), 297
[89] *Coke and Gas*, 1949, 273
[90] Ibid., 345, 395
[91] Int. Gas Union, Paper 3, "Choosing a type of retort"
[92] *Amer. Gas Ass. Mon.*, **31**, 21
[93] Ibid., **30**, 27
[94] Cf. Annual Reports, 1947, **32**, 38
[95] *Gas Research Board Comm.* GRB 51
[96] *Gas World*, **130**, 1940
[97] Scrotzky, B. G. A., *Power*, **93**, 78

TAR AND TAR PRODUCTS

By E. A. COULSON, M.A., D.Phil., D.Sc.

GENERAL interest attaches to a review[1] of the history and present state of tar distillation in Scotland by F. M. Potter, an authoritative discussion[2] by S. Robinson of the co-operative schemes (which have been worked by producers and distillers since 1920) for the disposal of tar and tar products, a report[3] of the progress of the Coal Tar Research Association (which is now actively operating its own research station at Gomersal, near Leeds), and some observations[4] by R. B. Robinson on the growing competition of certain petroleum-derived materials with the tar-distiller's products. A paper[5] which illustrates a significant tendency in the United States, where this competition is keener, may be mentioned here, since it describes a successful attempt by a firm primarily engaged in tar distillation to produce intermediates and fine chemicals from its own primary products.

A report[6] on the German low-temperature coal tar industry which is complementary to a previous report[7] on the high-temperature tar industry has appeared. Together these two reports furnish a complete picture of German tar technology and contain much useful technical material. The Alkali Inspector's report[8] for 1948 contains statistics relative to the United Kingdom tar industry which show that while the number of operating tar works has been almost halved in twenty years (at the end of 1948, 187 works were registered), in the same period the amount of tar annually distilled has increased by over a third to 2·2 million tons.

Tar distillation, pitch, creosote and road tar

The properties of road tars and the behaviour of tar surfacings have been discussed by A. R. Lee.[9] The significant properties are adhesion and viscosity but the durability is determined by the resistance to weathering and oxidation. In a series of papers[10] published work on the insoluble matters of coal tar has been reviewed and further light thrown on the nature of 'free carbon' fractions and the coal tar resins. Zinc has been detected in 'free carbon' and the presence of Pb, Fe, Co, Mn and other elements was indicated. A study[11] of the heat capacity and heat content of various types of tar and pitch has provided useful chemical engineering data for the solution of distillation problems and certain improvements in the efficiency of pipe-stills have been claimed and in the preparation of hard pitch and oils from medium soft pitch.[12,13] Efforts to find new applications for pitch continue and the possibility of employing it as a core binder in the foundry has been examined.[14] A useful modification of the heat sensitivity of pitch has been effected by the incorporation of 5% by weight of such a substance as polyvinyl chloride (mol. wt. > 5000). Thus a pitch originally of ring and ball setting point 53° C. had its setting point raised to 73° C. and was considerably less brittle (Fraas test) than an unmixed pitch of the same setting point. Claims for improved adhesion or durability have been made in connexion with other additives.[15] However, in present conditions much current production

of pitch and creosote will continue to be used as fuel and a newly issued specification[16] redefines the two grades of creosote hitherto sold under B.S. 503:1933 as furnace fuel, and the materials commonly described as creosote/pitch mixture.

Separation and purification of tar constitutents

The separation of tar constituents has a perennial interest and continues to excite effort in many different fields of work. Of 68 tar constituents for which the best values of the salient properties (density, melting point, boiling point, calorific value, specific heat, latent heats of fusion and vaporization, and refractive index) have been compiled,[17] almost all have at one time or other been on the market although of course the larger proportion are of no great commercial or technological value. Fresh effort applied to the improvement of methods for separating and purifying the plentiful staple products—benzene, phenol, naphthalene, etc.—would seem overdue and it should not escape the notice of the chemist whose primary interest is in tar products that unremitting effort applied to improving the separation and purification of such constituents of straight or processed petroleum fractions as benzene, toluene, the xylenes, styrene, etc., continues on the by now familiar lines of azeotropic fractional distillation, solvent extraction, etc.[18]

Neutral constituents

The preparation of the useful insecticide 'Velsicol 1068' from *cyclo*-pentadiene has stimulated further investigation[19] of the properties, reactions and applications of this constituent of benzole forerunnings. Improved methods of recovery[20] consist in dimerization by storage of the crude cut in absence of oxygen and at room temperature but in presence of a halide catalyst such as $SnCl_4$ or BF_3. The dimer is then separated by vacuum distillation and depolymerized when required by heating to 200–240° C. Two methods for determination of the purity of di*cyclo*-pentadiene concentrates have been given—one cryoscopic,[21] the other depending on the addition of formic acid to an ethylenic link and determination of the saponification value of the ester.[22]

The use of acetone to entrain paraffin impurities out of acid-washed benzene has been patented and it is claimed[23] that the finished benzene contains neither paraffins nor sulphur. An alternative method of refining benzene has been claimed[24] based on crystallization from a mixture of *iso*propyl alcohol and propane at about − 17° C., whereby 50–60% of the benzene is separated, followed by azeotropic fractional distillation of the mother-liquor. In a method for refining toluene to the nitration grade, olefines are removed by counter-current washing with a 30–50% (by volume) solution of toluenesulphonic acid in toluene. The reagent is corrosive to steel unless a small amount of sodium arsenite is added as an inhibitor.[25]

The removal of thiophen from benzene which is intended for hydrogenation is an old problem for which fresh answers have been found. Thus E. B. Maxted[26] removes the thiophen by filtration of the specimen through a bed of platinum black. Another method[27] consists in adding

aqueous-alcoholic alkali and fractionally distilling whereupon, it is claimed, only the benzene is entrained off by the alcohol and the thiophen is left in the residue.

Some slight variations have been introduced into the established methods for separation of xylene isomers. Thus it is claimed[28] that the preferential sulphonation of the *m*-isomeride is best done with 50–70% aqueous sulphuric acid in the theoretical amount, boiling at 85–95° C. under reduced pressure. Water and hydrocarbons distil off and the latter are returned to the system. Finally all the unsulphonated hydrocarbons are removed by distillation and the residue consists of pure *m*-xylene-sulphonic acid which is desulphonated in the usual way. In other claims[29] the use of pentane, *iso*pentane or ethyl or methyl alcohol as solvents for the crystallization at − 70° C. of mixtures containing *m*- and *p*-xylenes is said to greatly facilitate the crystallization of the pure *p*-isomeride. The separation of the *o*-isomeride is the subject of another patent.[30] What is claimed to be an improved infra-red spectroscopic method of analysis for mixtures containing the three xylenes and ethyl benzene has been described.[31] The uncertainty is 1%. A method based on ultra-violet absorption spectra appears to be equally accurate.[32]

Papers and patents dealing with the alkylation of benzene and its homologues, chiefly with the object of securing polymerizable monomers of which styrene is the prototype, continue to be very numerous but are considered as strictly outside the scope of this review. One or two papers dealing with the preparation of methyl homologues can be indicated.[33]

A general method for purifying aromatic hydrocarbons consists in applying a vapour phase treatment over a dehydrating catalyst containing Cr_2O_3, Al_2O_3, Fe_2O_3, etc. at 450–600° C. Thiophen, and other sulphur compounds, paraffins, naphthenes and olefines are thereby decomposed.[34]

It has been shown that 99% of the indene content and of the coumarone content of a coal tar naphtha can be secured by a solvent extraction process, the solvent used being glycol.[35]

In a statistical survey and review the enormous increase in the production of naphthalene and in the consumption of products derived from it during the past 30 years has been emphasized.[36] A modern tendency in the separation and purification of naphthalene is to make a fuller use of fractional distillation. It has been claimed that occluded oils (about 10%) can be removed from the crude centrifuged product by washing with xylol[37] and also that in the refining by fractional distillation there is some advantage in injecting liquid water into the vapours at the top of the fractionating column.[38]

In spite of the well known plentifulness of both α- and β-methylnaphthalene in tar fractions of boiling point about 240–244° C. attempts have been made to prepare one or both of the isomerides by methylation of naphthalene. D. Ll. Hammick and his pupils[39] found that naphthalene and dimethyl ether reacted over bauxite to give an optimum yield of about 7% of mixed methylnaphthalenes at 200–300° C. and 50–70 atm. The ratio of α- to β-isomeride was about 4 : 1. Another set of workers reported[40] that the β-isomeride, substantially pure, could be obtained by interaction of the same reagents at temperatures between 200 and 700° C. over an aluminium silicate catalyst.

Sulphur compounds in naphthalene intended for hydrogenation are troublesome catalyst poisons. One way of dealing with these contaminants is to perform a preliminary hydrogenation followed by an oxidation which has the result that the sulphur compounds are converted into non-toxic derivatives.[41]

The determination of naphthalene and its α- and β-methyl derivatives in kerosene or heavy naphtha by a spectroscopic method using characteristic absorption bands in the ultra-violet can, it is claimed,[42] be carried out with an uncertainty of only 0·2%. A polarographic method[43] for the determination of naphthalene is capable of estimating so small a quantity as 10^{-6} g. in a 0·5 c.c. sample of oil.

A review of work on the vapour pressure/temperature relationships of naphthalene, with some additional experimental data, may be noted.[44]

It is not obvious that there is any novel feature in a complicated method for the separation of mixtures of anthracene, phenanthrene and carbazole recently published[45] which depends on the use of solvent naphtha, toluene and pyridine bases as selective solvents. However, the use of *cyclo*-hexylamine in the crystallization of these crude mixtures appears to be both novel and definitely advantageous since, owing to its much greater solvent power for the carbazole and phenanthrene the anthracene content can be recovered in both high yield and purity.[46] Actually even better recoveries and higher purities can be secured, or so it is claimed, by allowing the constituents of crude anthracene cake to react with maleic anhydride in a solvent such as xylene or decalin at the boil.[47] The anthracene–maleic anhydride addition product is extracted with aqueous alkali, liberated by acidifying and decomposed by vacuum distillation with superheated steam at 230–260° c./27 mm. and by passage through a furnace at 400° c. The formation of this maleic anhydride addition product is the basis of an improved method[48] for estimating anthracene in crude anthracene cake.

As another variant of the orthodox methods which are used in the separation of the four main constituents of crude anthracene it has been proposed first to hydrogenate with a metallic sulphide catalyst at 275–300° c./40–60 atm. and convert the anthracene to the 9 : 10-dihydro-derivative.[49] The hydrogenation product is then fractionally distilled and the dihydroanthracene is thus separated from the phenanthrene in distillate fractions, fluorene is obtained as fore-runnings and carbazole left in an undistilled residue : or the carbazole may be left as an undissolved residue if the hydrogenated anthracene cake is extracted with xylene before fractional distillation.

Acenaphthene has in recent years acquired an interest as the source of the polymerizable monomer acenaphthylene. The best way of obtaining the latter is by catalytic dehydrogenation[50] but an alternative process[51] consists in oxidizing the acenaphthene with Pb_3O_4 in acetic acid to 1-acetoxyacenaphthene which gives the acenaphthylene when pyrolyzed at 520° c. in presence of CO_2.

Sulphur compounds

The separation of carbon disulphide from hydrocarbons, especially from benzene or fore-runnings, is usually effected by the well-known

Y.T.D. method. It is now suggested[52] that aqueous mixtures of bases, containing, for example, *cyclo*hexylamine and α-picoline as well as caustic soda are very effective in removing carbon disulphide. From a benzene containing 9% of carbon disulphide the mixed reagent removed 99·5% of the carbon disulphide content. The carbon disulphide can be recovered from the aqueous extract by acidifying and distilling.

A very extensive literature survey[53] covering the reactions between H_2S, S and mercaptans on the one hand and unsaturated hydrocarbons on the other has permitted conclusions to be drawn regarding the mechanism of formation of S-containing sludges in wash-oils.

Tar bases

It is rather surprising that, judging from the output of papers and patents, more work is being applied at present to such relatively minor constituents of tar as the bases than to the far more plentiful phenols or hydrocarbons. This is a recent development; interest in tar bases was scarcely stimulated by an increased use of pure pyridine consequent upon the discovery of M. & B. 693 and only began to grow when it appeared that β-picoline and quinoline could find outlets as intermediates for the preparation of nicotinic acid. It can hardly be doubted that there are other potentialities in this group which time will reveal; meantime there is still considerable scope for ingenuity in devising separation and analytical processes in the groups of pyridine, quinoline and *iso*quinoline homologues.

The separation of aniline from tar base fractions containing also tertiary cyclic bases can be effected by azeotropic distillation; using a paraffin of suitable boiling point the aniline can be entrained.[54] An improvement[55] in the recovery of pyridine bases consists in controlling the p_H in the 'saturator' to between 8 and 9 thus avoiding emulsification. In view of the frequent use of pyridine perchlorate for purification or analytical purposes attention is drawn to a serious explosion after the use of this salt.[56] A new and specific colorimetric method for the estimation of pyridine is based on the reaction with chloroform in alkaline solution.[57] The hydrogenation of pyridine over a platinum catalyst is facilitated by the presence of acid: this is explained by the conversion to the unadsorbed pyridinium form.[58]

An extremely pure specimen of α-picoline (99·85 mols.%) has been isolated from coal tar bases by fractional distillation and the physicochemical properties, which included freezing point, boiling point, density and coefficient of expansion, viscosity, refractive index, dipole moment and the ultra-violet and infra-red absorption spectra, measured with considerable accuracy.[59]

The separation of the constituents of 'commercial β-picoline,' a base fraction b.p. approx. 140–144° C. which contains pyrrole and its derivatives as well as β- and γ-picoline and 2 : 6-lutidine, has given rise to much investigation and still excites interest. Pyrrole may be recovered from the fraction by adding sufficient caustic potash to form the potassio-derivative and then entraining away the pyridine homologues by fractionally distilling in presence of toluene. The pyrrole in the residue is liberated by addition of water, purified from traces of the pyridine homologues by

treatment with oxalic acid and finally distilled.[60] An effective way of removing 2 : 6-lutidine from this tar base fraction is by crystallization of the urea complex.[61] It has also been claimed that β-picoline is the only constituent which reacts readily with 2 : 4-dinitrochlorobenzene and that it may be separated and recovered by use of this reagent[62] although, to be sure, the quaternary dinitrophenylpyridinium chloride is not easily decomposed into its constituents. A much more straightforward procedure is to convert these base fractions into hydrochlorides and fractionally distil.[63] There are said to be sufficient differences in the boiling points (β-picoline hydrochloride b.p. 233° c., γ-picoline hydrochloride b.p. 240° c., and 2 : 6-lutidine hydrochloride b.p. 245° c.) to make the separation by fractionation reasonably good in a good column, but it will be realized that these hydrochlorides are extraordinarily corrosive to metal equipment.

Alternative methods permitting recovery of pure β-picoline turn on the use of reagents for the removal of γ-picoline and 2 : 6-lutidine, such as a mixture of acetic and phthalic anhydrides at 160–180° c. for 5 hr.,[64] or acetic anhydride and benzaldehyde or furfuraldehyde at 150° c. for 5 hr.[65] In either event the β-picoline is distilled or steam-distilled from a higher-boiling residue in which the unwanted components have been combined.

Various ways of oxidizing β-picoline or other alkyl-pyridines, -quinolines or-*iso*quinolines to pyridine carboxylic acids have been tried ; aerial oxidation at 400° c. over such catalysts as V_2O_5 or $V_2O_5 + Fe_2O_3$ is effective with β-picoline and certain other bases,[66] although the claim has been made that when mixtures of β-picoline and lutidiness are oxidized by air over $V_2O_5 + Cr_2O_3$ on pumice at 400° c. the lutidines are preferentially oxidized and the concentration of β-picoline in the product is increased.[67] Another general method[68] uses sulphuric acid with a small amount of a dissolved Se compound such as $SeOCl_2$ or H_2SeO_3 ; in still another[69] the β-picoline or other base is oxidized in aqueous phosphoric acid solution with 70% nitric acid added in portions.

No entirely satisfactory synthetic method for the preparation of pyridine homologues has yet been described ; yields by known methods are low and the products are complex. Pyridine can be methylated in the vapour phase by passage along with methanol over activated alumina, or aluminium silicate, at temperatures up to 500° c. but the product contains as preponderant constituent only an 8% yield of β-picoline. Unfortunately the catalyst is very rapidly poisoned and must be re-activated by heating in air or oxygen. Small yields of the pure β-picoline are claimed from the reaction between glycerol, ammonia and urea over alumina or aluminium silicate.[70] Claims to the production of β-picoline[71] by interaction of acrylic acid and ammonia at 400–500° c. over a dehydration–dehydrogenation catalyst (such as one or more of the metals Ni, Co, Cu, or Ag intimately mixed with one or more of the oxides of Al, Si, Zr, Th, or the rare earths) and to the production of alkyl pyridines in general[72] have been made : as an example of the latter process may be cited the production from acetaldehyde and ammonia, by passage over silica gel (98·5%) activated with alumina (1·5%) at 400–550° c., of yields of 20·4% α-picoline, 17·6% γ-picoline and 10·4% higher pyridine homologues.

A new use for polymethyl pyridines, in particular for 2 : 6-lutidine and tar base fractions b.p. 160–200° c. which consist of these pyridine homologues, is as corrosion inhibitors, in conjunction with alkylene glycols used as engine coolants.[73] There is little progress to report on the separation of these mixtures of higher pyridine homologues into individual constituents ; 3 : 5-lutidine is said to react specifically with 2 : 4-dinitrochlorobenzene[62] and *s*-collidine can be conveniently separated by crystallization of the hydrochloride.[74]

One or two of the new addition compounds reported to be formed between quinaldine and phenol and its homologues are sufficiently high-melting to be useful as a means of separating quinaldine from the mixture of bases—quinoline and *iso*quinoline—with which it is naturally associated[75]; the compound with *o*-cresol melts at 75° c. and that with *m*-4-xylenol at 51° c. A supplementary procedure for removal of *iso*quinoline from these mixtures consists in precipitating it as a complex with calcium chloride.[76] A base fraction of suitable boiling point is admixed with saturated aqueous calcium chloride and cooled and the precipitate is washed from adherent base with toluene, decomposed by treatment with water and the *iso*quinoline which then separates is dried and distilled. By exhaustive crystallization and fractional distillation in alternation a sample of coal tar *iso*quinoline was secured 99·5% pure and the important physico-chemical properties (b.p., f.p., density and coefficient of expansion, refractive index, dipole moment, and ultraviolet and infra-red absorption spectra) placed on record.[77]

When quinoline and *iso*quinoline are fully hydrogenated there are obtained (as would be expected) *cis* and *trans* forms of decahydroquinoline[78] and of decahydro*iso*quinoline[79] ; the latter were separated by crystallization of the mixed picrates.

One or two interesting new reactions of pyridine and quinoline bases have been studied. By interaction of γ-picoline and sulphur short chain compounds with structures derived from 2, 3 or 4 γ-picoline residues were built up.[80]

A new colour reaction of carbazole has attracted attention[81] and has been applied, with the use of a photoelectric absorptiometer, to the determination of carbazole in crude anthracene. With careful attention to the detail of the method the results can be brought within $\pm$ 10% of the carbazole content of the specimen. The colour, red-blue, is developed with salicylaldehyde in acetic–sulphuric acid solution when interaction occurs with the anthracene–carbazole sample dissolved in chloroform ; the extinction is measured after further dilution with acetic acid. Other known colour reactions such as those between carbazole and benzaldehyde, *p*-benzoquinone or *m*- and *p*-nitrobenzaldehyde have not yielded a satisfactory colorimetric method for determining carbazole in samples of crude anthracene.

The presence of small amounts of aniline, toluidines and xylidines in tar bases is of no great importance but the xylidines have long been available in the form of mixtures obtained by the mononitration of mixed coal tar xylenes and subsequent reduction of the mixed nitro-compounds. During the last war mixed xylidines acquired importance as an anti-knock additive for high-performance aviation spirit and there was a

considerable production in the United States. The separation of the chief individual components of these mixtures is not very difficult; *m*-4-xylidine is crystallized as the acetate, *p*-xylidine as the hydrochloride. Recent further developments[82] consist in treating the residues from the above-mentioned separations by vacuum fractionation, and crystallization of a fraction b.p. > 97° C./10 mm. to furnish *o*-4-xylidine: and also in treating residue from the recrystallization of *p*-xylidine by vacuum fractionation whereby fractions comprising mainly *m*-2-xylidine were secured and further purified as the formyl derivative.

Tar phenols

Greater attention is now paid to the recovery of phenol from waste liquors, especially from the ammonia liquors of by-product coke-ovens, than was the case when the supply of natural phenol exceeded demand. The subject of phenol recovery has recently been reviewed.[83] It has been found in practice advantageous to increase the free ammonia content before extracting these liquors with an organic solvent, e.g. benzole.[84] This has a two-fold effect: it diminishes the amount of hydrogen sulphide and other contaminants which are extracted with the phenol, and the amount of caustic soda solution required to strip phenol from the extract is lessened.[85]

The rectification of coal tar phenols in continuous equipment is still rather exceptional although it is known that a well-known continental firm of plant manufacturers has developed a successful continuous vacuum distillation unit for crude tar phenols which is controlled by an automatic regulation of the ratios of feed to reflux and to take-off on individual columns.[86]

A new and ingenious method of separating phenols from tar oils without the use of caustic soda has been patented.[87] Numerous unsuccessful attempts to avoid the use of caustic soda, and the attendant complications which have become traditional in the extraction of phenols, are on record. For the new method it can be said, from such scanty detail as the patent makes available, that the process appears to be technically feasible and not hopelessly uneconomic. The principle of the proposed method is that by careful fractionation of tar oils containing phenols, the phenols are largely segregated into particular fractions which are then subjected to azeotropic fractional distillation in the presence of water. The hydrocarbon content of the fractions is thus entrained away from residues which are substantially pure phenols. It is obvious that there is the possibility of effecting the separation of individual phenols by the method and indeed it is claimed that 85% of the carbolic acid content of a tar-oil fraction b.p. 170–175° C. can be secured in a purity of 95·56% in one batch operation.

A review[88] of the production of phenol in the United States makes interesting reading, especially a section dealing with the technicalities and economics of the three established industrial synthetic processes. The most economical process is that in which benzene is monochlorinated and the product hydrolysed; the least economical is the original process through the sulphonation of benzene. New data useful in the design

of plant for the recovery of phenol from weak aqueous salt solutions (such as must be handled in the chlorination-hydrolysis process) have been placed on record.[89] However, it now seems quite within the bounds of possibility that the direct oxidation of benzene to phenol with air or oxygen may become technically and economically possible. One group of workers have reported[90] yields at 604° c. of 43 to 56·5%, using a trace of iodine as catalyst: another group obtained smaller yields (of the order 32%) and found that although a small concentration of some such compound as *n*-hexene, *cyclo*-hexene, tetralin or diethyl ether (0·2 to 3·0% by volume) was effective in improving the conversion, other conditions—the reaction temperature, contact time, partial pressures of O_2, N_2 and benzene, total pressure in the system—were critically inter-related.[91] The effective recovery of the phenol from these products of aerial oxidation posed a number of problems.[92]

The results of a study[93] of the reduction of phenol to benzene over a molybdic oxide catalyst at least throw some light on the nature of the catalyst and its *modus operandi*.

Attention may be drawn to the re-issue of a number of British Standard Specifications dealing with coal tar phenols namely 1948 : 523, phenol; 1948 : 521, cresylic acid of specified *m*-cresol content, 5 grades; 1948 : 517, cresylic acid of specified *o*-cresol content; 1948 : 522, *o*- m- and *p*-cresol; 1948 : 524, cresylic acid, 6 grades.

The separation of *m*- and *p*-cresol from the close-boiling cut in which they occur is a problem that has fascinated very many workers and although one or two quite adequate (if not cheap) procedures have been devised, claims for new ones continue to be made. Fresh vapour pressure/temperature data[94] for a number of phenols, including *m*- and *p*-cresol and mixtures of these two isomerides yielded no evidence of azeotrope formation so that in principle at least, in spite of the closeness of the boiling points, the isomerides could be separated by straight fractional distillation. A fairly thorough-going attempt to find either azeotrope-formers or selective solvents which might facilitate this separation was without any useful result,[95] although many different substances—hydrocarbons, glycols, ethers—were tried and 28 *y*, *x* curves with the two cresols were plotted. A little success attended fresh attempts to find suitable high-melting complexes. Thus it was found that benzidine forms a promising crystalline compound with *p*-cresol but not with *m*-cresol, 2 : 6-lutidine forms a compound with *m*-cresol which can be applied to its separation from commercial 55–60% *m*-cresol mixture, and *p*-cresol forms compounds with γ-picoline or 2 : 3 : 6-trimethylpyridine which can be used for a similar purpose.[96,101]

Before leaving these lower homologues mention may be made of two papers on the colorimetric analysis of phenols in this group. The colour developed by 2 : 6-dibromoquinone-chloroimide with the phenol in a borate buffer may be measured photoelectrically at about 6700A. and used for the determination of phenol, *o*- and *m*-cresol.[97] A method for the analytical determination of *m*- and *p*-cresol in mixtures depends on the difference in absorption measured photoelectrically at 4920A. of the colours produced by nitrosation of the isomers.[98] The technique requires the construction of calibration curves from pure components and from

mixtures of known composition for comparison with measurements on mixtures of unknown composition.

The melting points and boiling points/12 mm. for the four commoner xylenols which had been subjected to exhaustive fractional distillation and crystallization have been recorded.[99] Two rather inaccessible coal tar phenols, *o*-3-xylenol and 3-methyl-5-ethyl-phenol, have been made available in limited amounts.[100] The formation of a crystalline compound between *m*-4-xylenol and *m*-cresol has been applied both to the separation of the first-mentioned component from mixtures with *p*-xylenol and the separation of the other component from mixtures with *p*-cresol.[101]

Krüber has announced[102] the isolation from coal tar fractions of five phenols higher-boiling than the xylenol group: 2-methyl-4-ethyl-, 2-methyl-5-ethyl-, 2 : 4 : 5-trimethyl-, 3 : 5-diethyl-, and *o*-phenyl-phenol. Their b.p.'s range from 222° c. to 287° c. and the first two are new compounds.

It is a matter of common knowledge that high-boiling tar-acids, especially those derived from vertical-retort tar or from low-temperature tar tend to darken or redden when exposed to air and alkali. For some applications, e.g. in disinfectant emulsions or as wetting agents in caustic soda solution, this is undesirable. It has been found that the development of colour is due to certain dihydric phenols, catechol, resorcinol and their derivatives, which may be removed with boric acid, or destroyed by aerial oxidation.[103]

Primarily for their use in the manufacture of resins soluble in drying oils and which may be used in the compounding of lacquers, varnishes and paints, alkyl phenols are obtained by interaction of phenol with indene,[104] methylindenes,[105] styrene[106] and *iso*butene.[107] Preferential alkylation has been applied to the separation of phenol mixtures[108]: a xylenol fraction containing the close-boiling pair *p*-xylenol and *m*-4-xylenol was treated with *tert.*-butyl chloride and $FeCl_3$ in carbon disulphide solution. The product consisted of 2 : 4-dimethyl-6-*tert.*-butyl-phenol and unalkylated *p*-xylenol which are readily separated by fractional distillation.

The elimination of alkyl-groups containing $>$ 4 C-atoms (as olefines) from phenols occurs readily under the action of phosphoric acid catalysts.[109]

In conclusion, there are three general reactions of phenols on which work has been published which may be noted. Complete replacement of the OH-group by NH_2- will occur at a suitable temperature and pressure of ammonia in presence of a small amount of ammonium chloride.[110] In this way phenol may be converted to aniline, the cresols to toluidines, the xylenols to xylidines and so on. The value of the amination process lies in the possibility of transforming accessible phenols into bases which are otherwise relatively inaccessible (e.g. *s*-xylenol → *s*-xylidine). Thiophenols are obtained[111] by interaction of phenolic compound with hydrogen sulphide under pressure at 400–600° c. The catalyst may be activated bauxite or metallic oxides as ThO_2, ZrO_2 or ZnO. Quinol derivatives are obtained by persulphate oxidation of phenols followed by methylation and acid hydrolysis.[112]

References

[1] *Chem. Tr. J.*, 1949, **125**, 29
[2] Ibid., 507
[3] Ibid., 486
[4] Ibid., 507
[5] Shearon, W. H., Hall, H. E. and Stevens, J. E., *Ind. Eng. Chem.*, 1949, **41**, 1812
[6] Rhodes, E. O., *U.S. Bur. Min. Inform. Circ.* 7490
[7] Idem, ibid., 7409
[8] *Chem. Tr. J.*, 1949, **125**, 211
[9] Lee, A. R., Road Res. Tech. Paper No. 12 (H.M.S.O.)
[10] Green, S. J., and Ward, S. G., *J. Soc. chem. Ind.*, 1949, **67**, 422; Green, S. J. and Thakur, B., ibid., 423, 436; Green, S. J. and Mikharji, S. M., ibid., 438
[11] Hyman, D. and Kay, W. B., *Ind. Eng. Chem.*, 1949, **41**, 1764
[12] Mann, H. C. and Brown, L. S., Newton Chambers & Co., Ltd., B.P. 608,301, 608,303, 619,496 and 619,574
[13] Wilton, T. O., The Chemical Engineering and Wilton's Patent Furnace Co., Ltd., B.P. 616,730 and 619,230
[14] Shportenko, P. I., *Stal*, 1948, No. 3, 268; *J. Iron Steel Inst.*, 1948, **159**, 337
[15] N.V. de Bataaf. Petr. Maats, B.P. 602,582; Kay, E., I.C.I. Ltd., B.P. 617,466; Parker, A. and Levinovitsch, L., B.P. 615,212
[16] B.S. 1469
[17] Coulson, E. A. and Herington, E. F. G., *Coke and Gas* 1949, **11**, 14
[18] Engel, K. H., Allied Chemical and Dye Corpn., U.S.P. 2,445,944; Claussen, W. H., Powell, T. M., California Research Corpn., U.S.P. 2,434,395; Lake, G. R., Union Oil Co. of California, U.S.P. 2,432,771; Latchum, J. W., Connors, J. S., Phillips Petroleum Co., U.S.P. 2,434,322; U.O.P. Co., B.P. 613,770; Birch, S. F., Collis, C. B., Anglo-Iranian Oil Co., B.P. 613,867; Standard Oil Development Co. and Röhm and Haas Co., B.P. 607,945 and 607,949; Clark, C. R., Allied Chemical and Dye Corpn., U.S.P. 2,385,610, 2,388,040 and 2,397,839.
[19] Velsicol Corpn., B.P. 614,931; Bruson, H. A., Resinous Products and Chemical Co., U.S.P. 2,382,037-8, 2,385,787–8, 2,389,136 and 2,393,607
[20] Carnegie Illinois Steel Corpn., B.P. 606,112; Sowter, P. F. C. and Rogerson, W. A., B.P. 612,893
[21] Ray, G. C., *Analyt. Chem.*, 1948, **20**, 331
[22] Bergmann, F. and Japhe, H., ibid., 146
[23] Gould, D. F., Allied Chem. and Dye Corpn., U.S.P. 2,389,041
[24] Keeling, W. O., Koppers Co. Inc., U.S.P. 2,438,368
[25] Shipley, G. H., junr. and Wilson, G. W., junr., Standard Oil Dev. Co., U.S.P. 2,436,494
[26] Maxted, E. B., *J. chem. Soc.*, 1948, 1091
[27] Carnegie Illinois Steel Corpn., U.S.P. 2,427,988
[28] Cole, P. J., Allied Chemical and Dye Corpn., U.S.P. 2,393,888
[29] Greenburg, R. B., Allied Chemical and Dye Corpn., U.S.P. 2,398,526; McArdle, E. H., and Mason, D. M., Standard Oil Development, Co., U.S.P. 2,435,792 and B.P. 585,076
[30] Koppers Co. Inc., B.P. 608,266
[31] Kaye, W. I., and Otis, M. V., *Analyt. Chem.*, 1948, **20**, 1006
[32] Tunnicliff, D. D., Brattain, R. R. and Zumwalt, L. R., *Analyt. Chem.*, 1949, **21**, 890
[33] Given, P. H., and Hammick, D. L., *J. chem. Soc.*, 1948, 2154; Hardy, D. V. N., *J. Soc. chem. Ind.*, 1948, **67**, 81, 150
[34] Carnegie-Illinois Steel Corpn., B.P. 618,447
[35] Gauger, A. W. and Breston, J. N., *J. Inst. Petrol.*, 1948, **33**, 687
[36] Skeen, J. R., *Chem. Engng. News*, 1948, **26**, 2555, 2894
[37] Société pour l'Exploitation des Procédés Ab-der-Halden, B.P. 611,213
[38] van der Hoeven, B. J. C., Koppers Co. Inc., U.S.P., 2,440,707; cf. B.P. 620,753
[39] Armstrong, G. P., Grove, D. H., Hammick, D. Ll. and Thompson, H. W., *J. chem. Soc.*, 1948, 1700
[40] Chatt, J., Crundall, S. F. W. and Cullinane, N. M., Peter Spence & Sons Ltd., B.P. 611,551
[41] Maxted, E. B. and Walker, A. G., *J. chem. Soc.*, 1948, 1916
[42] Coggeshall, N. D. and Glessner, A. S., *Analyt. Chem.*, 1949, **21**, 550

[43] Thornton, D. P., junr., *Petrol. Process.*, 1948, **3**, 673
[44] Sears, G. W. and Hopke, E. R., *J. Amer. chem. Soc.*, 1949, **71**, 1632
[45] Bojanowski, J., Seniów, S. and Jedrysik, H., *Przem. Chem.*, 1948, **27**, 285
[46] Hatton, J. P., May, R. and I.C.I. Ltd., B.P. 611,554
[47] Insinger, T. H., junr. and Koppers Co. Inc., U.S.P. 2,440,688
[48] Ubaldini, I., Crespi, V. and Guerrieri, F., *Ann. chim. appl. Roma*, 1949, **39**, 77
[49] Corson, B. B., Detrick, R. S. and Koppers Co. Inc., U.S.P. 2,438,148
[50] Jones, J. I., *J. Soc. chem. Ind.*, 1949, **68**, 225 ; Jones, J. I. and Kynaston, W., ibid., 228.
[51] Flowers, R. G. and General Electric Co., U.S.P. 2,390,363
[52] Milner, D. W., Holdsworth, E. C. and Y.T.D. Ltd., B.P. 617,969
[53] Hoffert, W. H. and Wendtner, K., *J. Inst. Petrol.*, 1949, **35**, 171
[54] Milner, D. W., and Y.T.D. Ltd., B.P. 598,882
[55] Wells, J. H. and Wilson, R. J., junr., U.S.P. 2,435,663
[56] Zacherl, M. K., *J. Text. Inst., Manchr*, 1948, **39 A**, 388
[57] Ploquin, M. J., *Bull. Soc. Chim.*, 1947, **14**, 700
[58] Maxted, E. B. and Walker, A. G., *J. chem. Soc.*, 1948, 1093
[59] Freiser, H. and Glowacki, W. L., *J. Amer. chem. Soc.*, 1948, **70**, 2575
[60] Engel, K. H., Allied Chemical and Dye Corpn., U.S.P. 2,388,475
[61] Riethof, G., Pittsburg Coke and Iron Co., U.S.P. 2,376,008
[62] Lukes, A., *Coll. Czech. Chem. Comm.*, 1947, **12**, 263
[63] Cislak, F. E., Cunningham, O. D. and Reilly Tar and Chemical Corpn. Inc., U.S.P. 2,374,418
[64] Riethof, G., Pittsburg Coke and Chemical Co., U.S.P. 2,443,479
[65] Idem, U.S.P. 2,388,499
[66] Cislak, F. E., Wheeler, W. R. and Reilly Tar and Chemical Corpn., U.S.P. 2,437,938
[67] Polyakova, I. M., *J. appl. Chem., USSR*, 1947, **20**, 845
[68] Mueller, M. B., Allied Chemical and Dye Corpn., U.S.P. 2,436,660
[69] Cislak, F. E., Wheeler, W. R. and Reilly Tar and Chemical Corpn., U.S.P. 2,396,457
[70] Cullinane, N. M., Chard, S. J. and Meatyard, R., *J. Soc. chem. Ind.*, 1948, **67**, 142
[71] Phillips Petroleum Co., B.P. 610,987
[72] Idem, B.P. 609,059
[73] Sexton, A. R., Dow Chemical Co., U.S.P. 2,441,848
[74] Engel, K. H., Allied Chemical and Dye Corpn., U.S.P. 2,426,442
[75] Cislak, F. E., Otto, M. M. and Reilly Tar and Chemical Corpn., U.S.P. 2,432,064
[76] Riemers, F. E. and Allied Chemical and Dye Corpn., U.S.P. 2,391,270
[77] Freiser, H. and Glowacki, W. L., *J. Amer. chem. Soc.*, 1949, **71**, 514
[78] King, F. E., Henshall, T. and Whitehead, R. L. St. D., *J. chem. Soc.*, 1948, 1373
[79] Witkop, A., *J. Amer. chem. Soc.*, 1948, **70**, 2617
[80] Thayer, W. M. and Corson, B. B., ibid., 1948, **70**, 2330
[81] Strafford, N. and Stubbings, W. V., *Rec. Trav. Chim. Pays-Bas*, 1948, **67**, 918. [*See also* Coulson, E. A. and Biddiscombe, D. P., *Analyst*, 1949, **74**, 46]
[82] Birch, S. F., Fidler, F. A., Dean, R. A., Anglo-Iran Oil Co., Ltd., B.P. 619,873
[83] Coxon, W. F., *Gas Times*, 1948, **54**, 42; *B.C.U.R.A. Mon. Bull.*, 1948, **12**, 18
[84] Koppers Co. Inc., B.P. 605,635
[85] Gollar, H. A. and Koppers Co. Inc., U.S.P. 2,445,825
[86] Société pour l'Exploitation des Procédés Ab-der-Halden, B.P. 619,857
[87] Milner, D. W. and Y.T.D. Ltd., B.P. 595,406
[88] Messing, R. F. and Keary, W. V., *Chem. Industr.*, 1948, **63**, 43, 234
[89] Bogart, M. J. and Brunjes, K., *Chem. Engng. Progr.*, 1948, **44**, 95
[90] Porter, F. and Solvay Process Co., U.S.P. 2,392,875 ; Harman, R. A. and Solvay Process Co., U.S.P. 2,382,148
[91] Krieble, R. H., Denton, W. I. and Socony-Vacuum Oil Co. Inc., U.S.P. 2,440,233–4 and 2,439,812
[92] Porter, F., Allied Chemical and Dye Corpn., U.S.P. 2,437,921
[93] Woodward, L. A. and Glover, A. T., *Trans. Faraday Soc.*, 1948, **44**, 608
[94] Goldblum, K. B., Martin, R. W. and Young, R. B., *Ind. Eng. Chem.*, 1947, **39**, 1474
[95] Othmer, D. F. *et al.*, ibid., 1949, **41**, 572
[96] Cislak, F. E., Otto, M. M. and Reilly Tar & Chemical Corpn., U.S.P. 2,432,062–3
[97] Ettinger, M. B. and Ruchhoft, C. C., *Analyt. Chem.*, 1948, **20**, 1191
[98] Savitt, S. A., Goldberg, A. M. and Othmer, D. F., ibid., 1949, **21**, 516
[99] Huckel, F. and Rothkegel, H., *Chem. Ber.*, 1948, **81**, 71.

[100] *Chem. Tr. J.*, 1949, **125**, 339
[101] Cislak, F. E., Otto, M. M. and Reilly Tar & Chemical Corpn., U.S.P. 2,456,581–2
[102] Krüber, O., *Chem. Ber.*, 1948, **81**, 221
[103] Bondy, H. F., Tunnicliffe, H. R. and Low Temp. Carb. Ltd., B.P. 621,639
[104] Soday, F. J., United Gas Improvement Co., U.S.P. 2,423,415
[105] Idem, U.S.P. 2,444,233
[106] Underwood, J. W. and General Electric Co., U.S.P. 2,432,356
[107] Basterfield, H. A. and I.C.I. Ltd., B.P. 616,829
[108] Luten, D. B., junr., de Benedictis, A. and Shell Development Co., U.S.P. 2,435,087
[109] Stilson, G. H., Fishel, J. B. and Gulf Research and Development Co., U.S.P. 2,383,279
[110] Birch, S. F., Fidler, F. A., Hardy, D. V. N. and Molloy, E. L., B.P. 619,877
[111] Ballard, S. A., Winkler, D. E. and Shell Development Co., U.S.P. 2,438,838
[112] Baker, W. and Brown, N. C., *J. chem. Soc.*, 1948, 2303

MINERAL OILS

By W. H. CROUCH

THE world crude-oil reserves[1] at the end of 1949 are estimated to be 76,637¼ million barrels, an increase of about 1500 million barrels over the amount estimated for 1948. The total world production of crude oil in 1949 is estimated at 940 million barrels.[1] The most significant trend in production is the increased output of the Middle East fields, which amounted to 20%, and the continued decline of the U.S.A. production in relation to world production: 62, 59 and 54·3% respectively for the years 1947, 1948 and 1949. World production increased by 10·2% of the previous year and the U.S.A. production dropped by about 9%.

The production of crude oils from new wells in the Sinai Peninsula, Suez Gulf area of Egypt is reported by D. M. Duff.[2] He discusses the possibility of large-scale developments, and gives information of the older producing wells in Egypt, Gemsa Hurghada and Ras Gharib, and data for the new wells as follows: Sudr crude oil has an American Petroleum Institute (A.P.I.) gravity of 23, and a sulphur content of 2·08%; Ras Matarma has an A.P.I. gravity of 19; Asl has an A.P.I. gravity of 22, and contains 2·09% sulphur. The crude oil from Wadi Feiran[3] has an A.P.I. gravity of 23. Asl is about 40 miles south of Suez, and is about 10½ miles from Sudr. Wadi Feiran is roughly 80 miles south of Asl; all are in the Sinai peninsula of Egypt.

The yield and properties of eight other Asiatic crude oils, the Arabian crudes, are given and discussed by W. L. Nelson.[4] Egloff reviews the Saudi Arabian Industry[5] and gives the yields and properties of the two main oils of Abqaiq and Damman: they are predominantly paraffinic in character; Abqaiq produces two-thirds of the Saudi Arabian production.

A review by Egloff[6] of the refining of South American crude oils and their properties includes those from Argentina, Colombia, Peru, Equador, Bolivia, Chile, Brazil, Venezuela, Costa Rica and Mexico. The properties of products from cracking also are shown for Mexican oils.

Production of crude oil in the Schoonebeck field, Holland, is discussed by W. Th. B. Reimering.[7] It has a specific gravity (A.P.I.) of 24·8, an average viscosity of 114·5 centistokes at 122° F., and a pour-point range from 43–54° F.; the sulphur content is approximately 6·6%. A rather stable water-in-oil emulsion accompanies the oil. The method of its breakdown is described.

Typical inspection tests on the new Alberta crude oils of Canada are given[8]: they cover specific gravity, pour-point, Engler fractions at 400°, 500° and 600° C., sulphur and salt contents. High sulphur and salt contents are found in the following: Lloydminster, 3·14% and 558 lb./1000 barrels; Bon Accord, 0·77% and 350 lb./1000 barrels; Barrhead, 2·23% and 2000 lb./1000 barrels: these are the heavier oils. The crudes from Leduc-Woodbend, Redwater, Schoep-Golden Spike, Imperial Whitemud, and Joseph Lake, have sulphur contents ranging from 0·52 to 0·20%, with far lower salt contents.

Natural gas

Important papers on natural gas have been published: (i) by R. L. Hock on 'Performance and efficiencies of a gas cycling operation,'[9] (ii) by F. J. Neslage entitled 'Relationship between gasoline plants and gas-repressuring programme,'[10] (iii) in 'Production from Condensate Reservoirs'[11] L. C. Stevens and B. P. Boot deal with the phase behaviour of condensate reservoir fluids and explain the significance of 'retrograde condensation.' The practical aspects of 'gas cycling' are discussed.

The presence of water in the transmission and processing of natural gas gives rise to many difficulties which are described by F. C. Risenfeld and H. D. Frazier[12]; the methods for removing the water and the apparatus for determining it are discussed, and a new analytical method for determining the water is described which gives the absolute water content.

Three new methods of storage of natural gas have been described: H. L. Fruechtenicht and J. B. Simpson described[13] the plant and lay-out and procedure by which propane–air and natural gas mixtures, of high B.Th.U.-value, are prepared and stored in a depleted natural gas formation; details are given of a method involving the use of a solid adsorbent fuller's earth for the storage of natural gas[14]; A. Antonelli[15] proposes, in order to face peak loads, to liquefy natural gas by an orginal method based on the expansion of the gas compressed in a pipeline and by the use of alcohol as an intermediate refrigerating agent.

Petroleum substitutes

A report issued by the U.S. Bureau of Mines[16] on investigations of oil production from various U.S. bituminous and sub-bituminous coals and N. Dakota lignite by an improved hydrogenation process, states that unlimited supplies of premium gasoline from coal can be marketed at only 3 to 4 cents/gal. above current prices. From a 30,000-barrel per day plant, from 20,250–22,500 barrels of gasoline, 1240 barrels of phenols and 6260–8150 barrels of liquid gases may be obtained. The gasoline has an octane number (O/N) of 74–78, with low sulphur content and higher aromatics and calorific value than those from crude oil. The liquid petroleum gas contains about 3% C_2, 65% C_3, $32\frac{1}{2}$% C_4 hydrocarbons. The phenols consist of about 20% carbolic acid and 45% xylenols. Diesel fuel of low pour-point and jet fuels of − 76° F. pour-point, passing specifications JP–1 and JP–3, can be provided.

E. V. Murphree[17] in a progress report on synthetic fuel production describes a new avenue for shale-oil conversion and gives the costs for production of 97 O/N (research method) gasoline from the following:

Gulf Coast petroleum	Natural gas	Colorado shale	Coal
14·5	12·5	21·5	19·0 cents/gal.

Total investment, raw materials, manufacturing and transport costs are also shown.

The Hydrocol synthesis is extensively described[18] in a progress report and review of the Carthage project at the Brownsville plant, Texas. Ninety million cu. ft. per day natural gas are used for making synthesis gas from which 6000 barrels of gasoline, 900 barrels of gas oil and 200 barrels of fuel oil per day are obtained. The oxygenated products from the synthesis will be processed by the Stanolind Company at Tulsa.

Hydrocol gasoline[19] from the fluidized iron catalyst by hydrogenation of carbon monoxide is a low-boiling and highly olefinic fuel with hydrocarbons consisting predominantly of straight-chain or single-branched olefines with the double bond in the 1-position in contrast to the high-boiling paraffinic product produced with the cobalt catalyst in the Fischer–Tropsch process. Its highly olefinic character permits conversion of both C_3 and C_4 and naphtha fractions to high-octane stocks that blend well with petroleum fractions.

Plant and process for synthesis gas production by the continuous re-forming of light hydrocarbons with steam and carbon dioxide are described.[20] Gases of varying hydrogen–carbon monoxide ratios of 1 : 3·7 and 1 : 9·85 represent operational limits imposed by the available carbon dioxide for re-former feed. 85–90% carbon monoxide is obtained.

A new synthesis of hydrocarbons—'Isosynthesis'—is described.[21]

Hydrogenation of carbon monoxide is carried out at 300–400 atm. and about 450° C. with a thorium oxide catalyst. Zirconium or cerium oxide can be employed and, to a less extent, alumina. Gaseous and liquid hydrocarbons are formed, in which the C_4 compounds are 80–90% *iso*-compounds. At 600 lb./sq. in. and 450° C. with ThO_2 the product consisted of 34·5% of liquids : 29·3%, *iso*-C_4 ; 14·7%, C_3 and *n*-C_4 ; and 18·2% of C_1 and C_2 hydrocarbons, besides dimethyl ether. If the temperature is below 400° C. and pressure above 600 atm., considerable amounts of oxygenated compounds are formed, mostly methanol, 1-butanol and dimethyl ether.

By percolation through silica gel, eight fractions, from a synthetic gasoline obtained[22] from synthesis gas with a fluidized iron catalyst, have been separated into paraffins, olefines, aromatic and oxygenated compounds. The following information was obtained on the gasoline fractions : (1) 40–50% of the C_7 C_6 and C_5 fractions consisted of straight-chain 1-olefines ; (2) the aromatic compounds identified were : benzene, toluene, the three xylenes, ethylbenzene, *n*-propylbenzene, *iso*propylbenzene, 1-methyl-2-ethylbenzene, 1-methyl-3-ethylbenzene, 1-methyl-4-ethylbenzene, *n*-butylbenzene, *iso*butylbenzene, 1 : 3-diethylbenzene and 1 : 4-diethylbenzene.

The approximate composition of Colorado shale oil naphtha is shown by J. S. Ball *et al.*[23] to consist of 30% paraffins and naphthenes, 40% olefines, 20% aromatics and 10% of sulphur, nitrogen and oxygenated compounds. The non-hydrocarbons are mainly in the form of thiophens, pyridines and phenols, respectively.

Refinery plant

The world-wide activities of the petroleum industry have continued during 1949. Refiners have invested millions of pounds in plant expansion and modification, and on research facilities and investigations. The refinery building programme is the largest ever known.[24] More than 150 building projects[25] are under way, including nine new petro-chemical installations.

A survey of world refineries[26] shows the total number as 667, excluding the U.S.S.R. The total crude oil and cracking capacities are given as 10,544,657 and 5,164,810 barrels per day.

Construction under way at a cost of £37½ million, will make the Fawley (Hampshire) refinery of the Anglo-American Oil Company the largest refinery in Europe.[27] It will process mainly Kuwait and other Middle East crudes at the rate of 110,600 barrels a day, and have a cracking capacity of 41,000 barrels per day.

G. Egloff has reviewed[28] the plant expansion and modification plans of the petroleum industry, together with the petro-chemical aspects. He shows the progress made over the years and discusses the improvements and trends in processing and products.

New plants for the production of chemicals from petroleum products, completed and under construction, are described in many papers.

The petroleum chemical plants in the south-western states of America are described and the main products manufactured are listed by R. F. Goldstein.[29]

At Partington, near Manchester,[30] Petrochemicals Ltd. have started operating the first of five Catarole plants for the production of rich olefinic gases and 70 different chemicals from non-aromatic charging stocks.

Scottish Oils Ltd.,[31] at Grangemouth in Scotland, have planned a refinery expansion programme costing £10 million and will spend £20 million on the adjacent chemical plant. Middle East crudes will be catalytically cracked, and selected gases and liquid fractions will be used for chemical production.

The Royal Dutch Shell group[32] are expanding their refinery at Pernis, Holland and adding plant for chemical production. The plans include a new 6000-ton/day distillation plant, a vacuum unit, a reforming unit, and a polyvinyl chloride plant, etc. Detergents will also be manufactured from operations on paraffin wax.

At Stanlow, near Chester,[33] the Shell group have started operating part of a new chemical installation. Gas oil will be thermally cracked, the rich olefinic gases segregated in a separating unit, and then treated in other units to produce a range of commercial solvents etc. including *iso*propyl alcohol and *iso*propyl ether, acetone, diacetone alcohol, mesityl oxide, methyl *iso*butyl ketone, *sec.*-butyl alcohol, methyl ethyl ketone, etc.

Imperial Chemical Industries Ltd.,[34] in an £80 million expansion programme, are spending £22 million on new construction at Wilton for the processing of petroleum products for chemical manufacture. Plant for the production of Perspex sheets and phenol–formaldehyde moulding powder and polythene will be increased. Propylene (for conversion to acetone, *via iso*propanol) hydrogen and methane (for Calor gas etc.) will be transported by pipe line to Billingham works for processing.

Plants under construction for manufacturing carbon black from petroleum products in England have been announced: at Ellesmere Port, Cheshire, England, the Carbot Carbon Co. Ltd.[35] expect to produce 10,000 ton/year carbon black from oil imported from the U.S.A.; Philblack Ltd.[36] expect production of carbon black by June 1950 at Avonmouth.

Refining processes and thermal cracking operations

The components and their allocation in a refinery-process cost-account are discussed by W. J. Jones.[37] Process-cost studies of alkylation and

polymerization,[38] hypersorption for propane-recovery[39] and thermal-reforming[40] operations were described at the American Institute of Chemical Engineers meeting at Tulsa in May, 1949.

The production of high-purity methyl*cyclo*hexane from straight-run heptane fractions[41] and the separation of hexane–hexene fractions into olefine and paraffin[42] by the Distex operation, are recorded.

Adiabatic and non-adiabatic rectification are discussed[43] as unit processes : (i) from the engineering aspect and (ii) as a heat process from the thermodynamic point of view. The method of calculating the number of heat-adding and heat-abstracting zones for continuous and batch operation and the calculation of the minimum number of rectifying plates required are described. The thermodynamic basis for assessing the minimum work required for both the rectifying methods is outlined.

The fundamental principles of extractive distillation are discussed[44] and a method is presented for the selection of a suitable solvent ; a simple method is given for estimating whether azeotropes are formed, and a method for evaluating relative effectiveness of different solvents is given.

Development of extractive distillation for toluene production and the separation of butadiene from butenes are described in another paper.[45]

The hydrocarbon azeotropes of toluene are recorded.[46] Tables of azeotropes and non-azeotropes are presented by L. H. Horsley.[47]

W. C. Edmister and D. H. Pollock[48] present a method by which the equilibrium flash-vaporization (E.F.V.) curves of petroleum fractions at various pressures may be predicted.

A correlation of A.S.T.M. 'true boiling point' and 'flash vaporization' curves covering 45 T.B.P. and 28 A.S.T.M. distillation curves, is recorded by W. L. Nelson and H. J. Harvey.[49]

A process is described[50] for the desulphurization of straight-run and thermally or catalytically cracked gasolines by means of a tungsten–nickel sulphide catalyst in the presence of hydrogen at 650° C. and 720-lb./sq. in. pilot plant operations show sulphur reductions of 0·26–0·002, 0·17–0·002, 0·065–0·001% ; 0·08–0·003% ; and 0·51–0·008% for the respective gasolines processed. The process has been used on a large scale to augment supplies of aviation gasolines.

Extraction of sulphur compounds with anhydrous liquid hydrogen fluoride shows an orderly progression with changes in molecular weight. Besides extraction, certain sulphur compounds undergo intra- and inter-molecular reactions in the presence of hydrogen fluoride. With mercaptans that are extractable with difficulty, the addition of olefines results in the formation of thio-ethers soluble in hydrogen fluoride ; this markedly enhances the degree of extraction.[51]

The steady and increasing demand for propane has called forth many papers relative to its recovery. Process design to increase its production is discussed in a series of papers by A. S. Glendening and C. F. Sanderson.[52] Propane recovery is also discussed by D. P. Thornton,[53] who gives data from six natural gasoline plants. High recovery of propane in other plants is recorded by M. E. Garrison[54] and by M. S. McAllister.[55] The economics and engineering problems of propane recovery are described by F. G. Noble.[56]

A greatly simplified process for the recovery and the separation of ethane and propane as used at Dubach, La., U.S.A., is described by C. B. Ames and T. D. Tabbert.[57]

The hypersorption process which employs a moving-bed of activated carbon to absorb light hydrocarbons from lean gas streams is described by Berg *et al.*[58] who give data of the separation of ethylene from feed streams, propane and nitrogen from natural gas, ethylene and hydrogen from refinery gas streams, and also the purification of synthesis gas, acetylene recovery from oxidation gases, separation of methane and hydrogen chloride, and purification of hydrogenation gases.

Rich-oil stabilization for the removal of methane and ethane from the circulating stream in an absorber, while retaining the propane and higher hydrocarbons, is explained. Types of plant employed and tabulated results of operations are described by S. Godblatt and H. M. Nelly.[59]

Data of hydroforming and thermal reforming operations on sweet and sour heavy straight-run naphthas are given by N. H. McLaurin, C. H. McIntosh and D. S. Kaufman,[60] covering product distribution, yields and octane-number relationships. The relative economics of the two processes, on both feed stocks, are shown.

Extensions and developments are reviewed[61] of high-temperature, low-pressure vapour-phase cracking of petroleum, natural gas and certain refinery 'off-gases' for the production of low molecular weight olefines for the chemical industry.

A new cyclic adsorption process is described[62] by which an almost quantitative separation of aromatics and olefines from the other components of many feed stocks of wide boiling-range, is obtained. The yields and purity of the products are higher than those of the products from conventional solvent extraction or acid treating methods. The premium kerosines, Diesel fuels, spray oils and lubricating oils are particularly outstanding.

The physical properties and characteristics of polyform distillates are described by W. C. Offutt, M. C. Fogle and H. Beuther.[63] They are rich in aromatics and low-boiling olefines and lean in high-boiling olefines, have high over-all volatilities and high octane numbers, and have excellent blending qualities. Catalytically treated, they produce good aviation base stocks.

The development of Middle Eastern petroleum resources has renewed refiners' interest in the Edeleanu process. P. Obergfell[64] discusses the application of the process to modern requirements and gives data relative to the treatment of naphthas, kerosenes, gas oils and Diesel fuels. A possible application is seen in the treatment of catalytic cracking recycle stock to remove the aromatics, thus increasing the capacity for virgin feed stocks.

H. McReynolds and J. M. Barron[65] present correlations of yields, product quality, sulphur distribution and fresh feed capacity developed for thermal cracking of many catalytically cracked cycle gas oils. Fluid catalytic cracked cycle gas oils are poorer cracking stocks than virgin gas oils, since they tend to yield more cycle gas oil than virgin gas oils and less naphtha than the corresponding virgin gas oils of the same gravity. In

general, the A.S.T.M. octane numbers of the gasolines are lower than those from the same gravity virgin gas oils.

Modern solvent-refining of lubricating oils is discussed in a series of articles by V. A. Kalichevsky.[66]

Equations of performance for the wax-sweating operation are recorded.[67] They are derived for the general case of arbitrary initial composition and express the compositions and melting points of the products as functions of the yields. A theoretical treatment of the effect of oil retention by the melting cake is also given.

H. Ter Meulen[68] describes the development of the wax-sweating process into a continuous process in which 70 tons of charge stock are in 23 different stages at any particular time.

G. Weber[69] describes a rotary pressure-filter which has been designed and tested. This new device functions as a mechanical wax sweater, charging slack wax cake from the cold pressing of wax distillate.

Emulsion deoiling of crystalline waxes is described[70]: the process employs a combination of chilling and emulsification with cold water, with separation of the oil–water component by means of an efficient centrifugal unit automatically controlled. It reduces the oil content of high-oil slack wax stock to a total of 5% in minutes as compared with hours for normal sweating operations.

The continuous contact coking process is described by A. H. Schutte and W. C. Offutt.[71] In this process a residual oil at 750–850° F. contacts at the top of the tower a relatively large flow of hot circulating coke which in the downward flow has a residence time of from 15–40 min. Less gas, less gasoline and 9–13% more gas oil and less coke are produced than by delayed cracking. Investment cost is about 60–80% of delayed coking cost, and process costs are also lower; there are no coke-removal expenses.

The U.O.P. autothermic cracking process[72] consists of re-forming propane, naphtha, natural gasoline or other volatile hydrocarbons in admixture with air. Supplementary gas to meet an emergency or a continuous supply can be easily obtained.

Details are given of the volume, specific gravity and calorific value of refinery gases from the Catarole process of the Manchester Oil Refinery supplied to augment the Manchester district supply of gas.[73] The arrangements made and the expected results are described. Calorific value and specific gravity of refinery gas increased to 1450 B.Th.U. and 0·87 respectively so that more producer gas was necessary to maintain a cal val. of 450 B.Th.U./cu. ft. Certain harmful impurities of the refinery gas were removed by oil scrubbing.

Catalytic cracking and other catalytic operations

Catalytic 'Pyrocission' differs from thermal or catalytic cracking in that temperatures of 700–800° C. are used with very small contact times and the oil is diluted with inert gas or vapour. Studies[74] are reported of the action of various catalysts in the pyrocission of mineral oils to produce gaseous mixtures of high olefine content and to obtain the maximum higher-olefine/ethylene ratio.

The use of steam with natural catalyst in the cracking of high sulphur

stocks has shown that addition of steam to the regenerated catalyst before its contact with oil hydrates the catalyst and prevents loss of activity by sulphur poisoning. A discussion is recorded of the variables causing poisoning and their control.[75]

A recently developed improved moving-bed—the 'Houdriflow'—catalytic process is described.[76] It differs from the T.C.C. process in that the catalyst is transported by flue gas, the catalyst/oil ratio is 4 : 8 which permits operation with stocks from 0–100% vaporized, and allows a reduction of reactor feed preparation equipment, since a major portion of reaction heat is supplied by the catalyst entering reactor. Simplification of regenerator is possible due to high catalyst recirculation rates.

The various refinery applications of the Houdriflow process are described,[77] and it is shown that coking and viscosity-breaking are the best methods for preparing cat-cracking feed stocks.

The catalytic effects in suspensoid cracking are described by C. H. Caesar.[78] In addition to the primary reaction of carbon-bond scission, secondary reactions such as isomerization, polymerization and alkylation appear to occur. The effect of the catalyst is to increase the octane number of the gasoline, reduce the percentage of olefines in the light fractions, and to increase butane production.

In the Mid-Continent, West Tulsa modernization programme a 'heat-balanced' catalytic cracking plant is included; it embodies a number of new features not previously incorporated in a single plant. Details of the modernization are recorded by D. G. Morgan.[79]

'Platforming,' a new U.O.P. catalytic re-forming process for improving straight-run and natural gasoline by means of a platinum catalyst, is described by E. F. Nelson.[80] Naphthenes are converted to aromatics, high-boiling paraffins to lower-boiling ones and low-boiling paraffins are isomerized.

The process, it is claimed, combines the best features of both hydroforming and thermal re-forming and a large gain in octane number and low volumetric loss results.

A correlation[81] shows the effect of operating variables on polymer yield and quality for non-selective polymerization for motor gasoline production. By employing a copper pyrophosphate catalyst with propylene and butylenes, it is shown that conversion of the olefines in the total feed increases with increase in catalytic activity and in reactor temperature, with decrease in olefine and total space velocity, and with decrease in weight ratio of propylene plus normal butylenes to *iso*butylene.

Data obtained in full capacity test runs of the Cycloversion plant at the Shell Company's Wood River refinery, California, are recorded by R. B. Tuttle.[82]

Process flow diagrams and description of a combination catalytic reforming and cracking plant of the Cycloversion type are given by H. A. Neal and C. B. Ames.[83] Besides re-forming the naphtha or the full range of motor gasoline production the plant is capable of cat-cracking 2000 barrels per day of kerosene or gas oil stock.

An entirely new way is described for desulphurizing vapours from a topping plant is used by the Continental Oil Company at Billings, Mont.[84] It consists of a secondary reactor, smaller than the main fluid catalytic

one and operated at a lower temperature. One regenerator serves both reactors.

Petroleum sulphur problems were discussed at the American Chemical Society's symposium in March 1949.[85] The processes discussed included: hydrodesulphurization, catalytic desulphurization and solvent extraction. The properties and reactions of sulphur compounds, effect of sulphur in petroleum fractions and sulphur content of various types of gasolines are discussed.

Combustion and related phenomena

The influence of diffusion and flame propagation is described by A. C. Gaydon and H. G. Wolfhard.[86] From data for stationary pre-mixed flames of hydrocarbons at various pressures they conclude that flame propagation is accounted for by diffusion of free atoms or radicals. The thickness of the reaction zone varies approximately inversely with the pressure, and the flame speed is independent of pressure, exothermic reaction begins at about 700–800° c. and time of passage through pre-heating zone is much less than the induction period for ignition at this temperature. The thickness of the reaction zone is related to the distance which free hydrogen atoms may diffuse against the gas stream.

G. Pannetier,[87] in studies of the mechanism of combustion, covers the determination of the limits of inflammability of mixtures of various gases, reactions between free radicals, etc. Data are given of the speed of propagation of flames in closed tubes for mixtures of methane or natural gas with air. The effect of the condition of the wall is described.

H. G. Wolfhard and W. G. Parker[88] discuss the evaporation of kerosene droplets in a fine spray burning in still air at room temperature. No significant evaporation occurs before the pre-heating zone of the flame, and this zone is very narrow, but there is sufficient time for the smaller droplets to vaporize and diffuse into the gases in this zone; thus an inflammable mixture is formed which maintains the flame front.

Equilibrium and rate phenomena associated with the vaporization of fuel before combustion in aircraft engines are described by G. G. Lamb and L. J. O'Brien.[89] A comparison is made between A.S.T.M. and theoretical batch distillations.

The mechanism, extent and basic purpose of atomization of liquid fuels are discussed. Methods of atomization and a pressure jet atomizer are described. Structure of atomized sprays and the factors affecting atomization efficiency are discussed by J. R. Joyce.[90]

The inflammability characteristics of oil–air mists from cutting oils, quenching oil and Diesel oil are described by J. H. Burgoyne and J. F. Richardson.[91] With mists from a saturated vapour/air mixture the lower limits of inflammability were 42–46 mg./l. air. They are of the same order as expected for the corresponding vapour of various pure hydrocarbons listed. The upper limits were four or five times the lower.

The conceptions of flash and fire points as applied to single liquids have been examined by J. H. Burgoyne and G. Williams-Leir,[92] and a number of values for the flash-point calculated. The inflammability of mixtures of *n*-hexane and Freon 12 have been determined and an inflammability diagram has been constructed. With the aid of a general diagram of the

same kind the influence of mixture composition, temperature and volatility on the inflammability of binary mixtures of the same type is discussed.

A new burner method is described[93] for the determination of low burning-velocities and the limits of inflammability. Burning velocity/composition curves for propane, *n*-butane and *n*-pentane down to their lower limits of inflammability are presented.

In a paper on the effect of light on the combustion of hydrocarbons, R. G. W. Norrish and D. Patnaik[94] show that slow combustion of hydrocarbons, in general, takes place by a kinetic process,—a chain reaction showing 'degenerate branching' (Semenov); the case of methane is cited to illustrate the point.

The combustion of gas–air mixtures, in which the gas concentration is below the ignition temperature, or the temperature of which is below the ignition limit, cannot take place in the form of a flame. Fire-clay activated with iron and manganese oxides is capable of producing complete combustion at the temperature and the high flow velocity at which the gases are exhausted from an I.C. engine.[95]

Basic studies on flame stabilization are reported by C. G. Williams[96] in which an independent examination was made of several variables while keeping constant, or eliminating, those variables not being studied. The variables studied were: air–fuel ratio, approach gas velocity, turbulence in the approach gas stream, flame stabilizer size and shape, and type of fuel (both coal gas and propane); runs were made to obtain blow-out limits. Photographs of the flame under different conditions were taken.

A literature survey on combustion by B. Lewis and G. von Elbe,[97] mainly for 1948, covers fundamental investigations on gaseous combustion in piston-type and jet-propelled engines, gas turbines, etc.

In papers on the combustion process in vitiated air J. Barr and B. P. Mulline[98] visualize the process in six separate stages linked together, and describe them. The effect of inlet air vitiation upon each is considered. A number of physical and chemical properties of vitiated air have been calculated and are given together with flame spectra of both unvitiated and vitiated flames. In Part II, the influence of vitiation on mixing by diffusion is considered. Experimental studies are reported and compared with a theoretical treatment of the laminar diffusion flame. In Part III, the effect of air vitiation upon the ignition delay of weak kerosene–air mixtures is described. The ignition delay was found to vary according to the inverse square power of oxygen concentration at a given temperature. Part IV covers tests to determine the effect of inlet air vitiation upon stability, flame length, combustion efficiency, in a conventional aero-gas turbine combustion chamber. In Part V, the results of the studies described in the other parts are applied to specific problems relating to the use of slave chambers in research and development, reheat combustion stabilizer design and industrial gas-turbines.

G. E. A. Godsave[99] reports some measurements made of burning rates in g./sec. of single drops of a series of commercial fuels and pure hydrocarbons; he discusses the investigation.

The mechanism of mixture formation and combustion in a Diesel engine are discussed by J. J. Broeze and C. Stillebroer.[100] They observe that

under-penetration, causing local over-richness, tends to produce soot. Over-penetration, the wetting of relatively cold walls, forms aldehydes and blue vapours. High volatility and high cetane number of the fuel contribute to under-penetration. Both these conditions are closely connected with the design as well as with the load, speed and temperature.

The electrochemical, oxidation and detonation processes which take place in an I.C. engine during combustion are reviewed in relation to marine engine corrosion by H. Bergenheim.[101] He suggests that on account of the presence of electrolytes in the cylinders, metal ions are released; if the electrical insulation of the ship has low resistance the released electrons are conducted away, with the result that they subsequently produce oxidation of the lubricating oil. Evidence supporting the hypothesis given is recorded.

Motor spirit and aviation gasoline

Engine-starting in cold climates can be greatly eased by continuously forcing a relatively wide cut mixture of volatile hydrocarbons of different boiling points into the manifold intake independently of the air stream.[102] A suitable mixture for the purpose contains the following hydrocarbons, both paraffin and olefine, which should embody a substantial amount of the *iso*-compounds: C_2 up to 5%; C_3 from 10–25%; C_4 from 15–45%; C_5 from 30–40%. There should also be 10–25% of C_6 to C_8 hydrocarbons.

The effect of additives on engine deposits is discussed by Albright, Nelson and Raymond.[103] They show that the engine variable is of greater magnitude than fuel variation. The significant fuel factor leading to deposits appears to be certain trace deposits, particularly from antioxidants in association with the aromatics and olefines.

Data are given describing and interpreting the antagonism of selected sulphur compounds towards tetraethyl lead (T.E.L.), in widely differing fuels.[104] The decrease in T.E.L. efficiency is found to be independent of the concentration and fuel octane number. The decrease is also constant, within experimental accuracy, for *n*-heptane blends containing thiol or disulphide sulphur when the component blended with the heptane is changed from *iso*-octane to toluene or *cyclo*hexane. Sulphides are less antagonistic toward T.E.L. in *cyclo*hexane–heptane blends than in the other fuels. Thiophenic sulphur appears to be least antagonistic in the *iso*-octane–heptane blends.

An informative paper by F. R. Banks[105] describes the influence of T.E.L. on engine design and performance. The paper fully describes the history and development of T.E.L., and discusses the problems associated with its use in gasolines, lead scavengers, American and British practice, and the effect of T.E.L. fuels on the engine and its parts. The non-positive valve rotator and the positive rotator have improved exhaust-valve conditions and increased their life. The opinion is expressed that to assist general scavenging of all cylinder deposits the combustion chamber should be designed for a fairly high degree of turbulence. Engines having high turbulence always appear to be cleaner.

D. Downs[106] describes an investigation into the lead distribution in a four-cylinder typical road vehicle engine and give details of the fuel and lead distribution in the two middle and the outer cylinders.

The relationship between inhibitor concentration and extent of stabilization of motor fuel is expressed algebraically by two general equations, whose applicability has been demonstrated on thermally and catalytically cracked gasolines with four antioxidants.[107]

Metal deactivators for protection of 'drive-away' and copper-sweetened gasolines and lubricating oils are described by R. W. Watson and T. B. Tom.[108] Their effect depends largely upon certain structural factors described.

The inhibition of deterioration of cracked gasoline during storage is described by C. J. Pederson.[109] Peroxidic initial oxidation products are formed by a series of free-radical chain-reactions. These compounds are converted into various mono-and polymeric oxygenated products. By reacting with the chain-propagating free radicals the gasoline antioxidants inhibit deterioration. Salts of multivalent metals, particularly copper, accelerate autoxidation if they are present; they should be removed or deactivated. Metal deactivators suppress the activity of the metal catalysts by converting them into chelate complexes, devoid of pre-oxidant catalytic activity.

R. B. Thompson, L. W. Druge and J. A. Chenicek describe[110] investigations into the effect of sulphur compounds on the stability of furnace fuel oil and doctor-sweetened gasoline in storage. From sludge and soluble gum determinations, they observe that free sulphur, disulphides and polysulphides promote sludge formation, that thiophenol is particularly effective in forming sludge, but that thiophens, aliphatic mercaptans and aliphatic sulphides show little effect. The effect of di- and polysulphides suggests a reason for the adverse action of doctor-sweetening. The removal of mercaptans by caustic methanol gives a product of enhanced stability.

Discussing the oxidation stability of T.E.L. and leaded aviation gasolines, E. L. Walters and C. J. Busso[111] state that the addition of 3 ml./gal. T.E.L. to base blends of varying inhibitor content causes a lowering in stability to about 15% of that of the unleaded fuel. The effect persisted in blends containing normal amounts of olefines, aromatics and inhibitors. Effect of T.E.L. is not simply proportional to concentration: 1·5 ml./gal. has almost as great an effect as 3 ml./gal.

E. L. Walters, H. B. Minor and D. L. Yabroff[112] discuss the application of methods of direct measurement of gasoline-deterioration products, gum, or peroxide, during ageing. Methods applied to the study of stability factor, composition, treatment, inhibition, catalysts and factors influencing antioxidant and de-activator behaviour are described.

A method is described[113] of supplying anti-knock quality to engines only when it is needed, that is at or near full throttle. The method of antidetonant injection is described, alcohol–water–T.E.L. being used.

On the subject of alcohol response, from tests on straight-run paraffinic gasolines from Arabian crudes, plus alcohol, it is shown that an increase of about one octane number is obtained for each 1% alcohol added.[114]

A complete combustion process is discussed from a motion picture study of knock.[115] From this work it is concluded that the type of knock occurring in spark-ignition engines originates as a self-propagating disturbance starting at a point in the burning or auto-igniting gases and

spreading out through the incompletely burned gases at rates as high as 6800 ft./sec.

Engine knock and molecular structure of the fuel is discussed by W. G. Lovell.[116] An empirical examination of the behaviour of paraffins, *cyclo*pentane, *cyclo*hexane, aromatic and straight-run olefines with respect to knock and relationship between knock and molecular structure is recorded. Knocking characteristics of paraffin hydrocarbons are shown in graphs of critical compression ratio at which knock begins, against number of carbon atoms in the molecule. From data where critical compression ratio, under one set of conditions is plotted against the same function in the same engine under another set of conditions, the paraffins show regular class behaviour in being the least sensitive. The sensitivity of the other classes to engine change is greater, and can be correlated with their molecular structure.

A series of tests on 76 commercial fuels by the A.S.T.M. research and motor methods, and by road tests in 89 cars by the C.F.R. Borderline method, is reported by L. A. McReynolds and W. W. Suderman.[117] The results show that the best average correlation with road testing is obtained when laboratory ratings are weighted between 60–75% research plus 40–25% road ratings. The resulting value is termed the 'weighted-index octane-rating.'

The use of a road octane-number of a gasoline is proposed[118] as a means of evaluating the relative anti-knock quality of motor gasolines. Correlation with laboratory ratings was achieved by the use of the equation

$$\text{Road octane No.} = 0{\cdot}54\ (\text{F–1 rating}) + 0{\cdot}46\ (\text{F–2 rating}).$$

A. Taub,[119] in papers on the possibilities of higher compression without high-octane fuel, considers the advantages of conserving petroleum reserves by using a larger proportion of crude oil for gasoline production; he describes several high-compression engines designed to operate on low-octane fuels. Suggestions are made for obtaining maximum economy and maximum compression ratio for present fuels and the reduction of octane requirement. The work and theories of Ricardo and Janeway with respect to combustion chamber design are described, and common factors for them are enumerated. It is important that the internal hot spots and high temperature of the exhaust valve in particular be eliminated or made innocuous.

D. B. Brooks and R. B. Cleaton[120] record the results of 18,957 engine ratings of 415 fuels made during 1942–46. Precision of rating and factors affecting precision, covering aviation motor and Diesel fuels, are described.

The fuel anti-knock requirements of engines are described by C. G. Williams.[121] Dealing with the trend towards increasing the basic thermal efficiency by using the highest possible compression ratio, he suggests the development of small high-speed Diesel engines rather than very high compression ratio engines requiring expensive high-grade fuels. Two methods (a bi-fuel system and anti-detonant injection) of taking advantage of the fact that octane requirement increases rapidly with decrease of load, are compared. The different octane requirements of side-valve and overhead-valve engines, influence of carburettor and inlet

manifold design on octane number needs, and the possibility of adopting fuel injection to individual cylinders, are discussed.

Experiments are described by R. O. King, W. A. Wallace and E. J. Durand[122] which show that conditions can be set up in which a reversal of the anti-knock effect of enriching a hydrocarbon–air mixture can be obtained in an unsupercharged engine. The reversal is of importance in respect of supercharged aero-engines in which it may occur before the mixture strength is increased to the value required for the development of maximum power. The results, considered in the light of the nuclear theory of detonation, indicate that the 'reversal' occurs when the rate of formation of finely divided carbon, by pyrolysis of the fuel, provides a pro-knock effect greater than can be offset by the anti-knock effects of the products of the high temperature heterogeneous oxidation reaction.

R. W. Wheeler and D. Downs[123] believe that the phenomenon of knock is essentially connected with the production of peroxides in the last part of the fuel-air mixture to be burnt.

D. Downs and A. D. Walsh[124] from their investigations of the effects of additives in experiments on aurally determined 'knock' found : (i) fuels may give rise to 'knock' by two mechanisms : a high-temperature process, as with benzene or methane, and the other a low-temperature process ; (ii) with benzene, methane or hydrogen as fuel, formaldehyde and nitrogen peroxide are strong pro-knocks, whereas in *iso*-octane, formaldehyde is an anti-knock, and nitrogen peroxide has a slight pro-knock effect ; (iii) methane and hydrogen both have considerable T.E.L. response.

R. O. King, W. A. Wallace and E. J. Durand,[125] discussing the causes of the anti-knock properties of rich mixtures, show that the anti-knock effect in the engine is increased by cooling if the enrichment of the mixture leads to an increase in the proportion of fuel admitted as liquid. *n*-Pentane and a commercial fuel containing high-boiling constituents were used in the experiments.

P. L. Cramer and J. M. Campbell[126] present a correlation of the knocking characteristics of liquid hydrocarbons in the Otto engine with previously published data on the initial reactions of ethyl radicals with representative paraffinic, olefinic, aromatic and hydroaromatic hydrocarbons. The correlation is discussed from the view point of a free radical mechanism based on the relative amounts and reactivities of the hydrogen atoms contained in the hydrocarbon molecule.

A. D. Walsh[127] shows that a correlation exists between the anti-knock effect of aromatic compounds and the influence of the side chains upon electronic properties of the benzene rings. Anti-knock effect increases with decreasing bonding of the ring electrons. The effect is exerted by the unchanged molecules and anomalies are explicable as due to pyrolysis or oxidation of the anti-knocks. The observed anti-knock effect of hexamethylbenzene suggests that the reaction between radical chain carriers and the benzene ring, which is responsible for inhibition by aromatic compounds, is best regarded as the temporary formation of a complex between the radical and the electronic cloud of the ring.

T. E. Taylor and H. J. Gibson[128] present a test procedure which is a new approach to the evaluation of engine warm-up as influenced by fuel

volatility. It is an attempt to express driver reaction on a sound technical basis. Tests showed that the 50% point had greatest bearing on warm-up of fuels and that the 10 and 90% points influenced the initial and final warm-up respectively.

A new technique is described for providing liquid fuel in solid form.[129] Plant-scale methods for preparing the solid product from petrol, urea–formaldehyde, ammonium thiocyanate, casein and Teepol are described

The physics and chemistry of hydrocarbon gels is discussed by E. K. Rideal.[130]

The specific heats of Napalm gasoline gels are recorded by G. O. Lanstroth and K. H. Hart.[131]

Hydrocarbons

Reports of the Hydrocarbon Research Group of the Institute of Petroleum have been published : (1) 'A general introduction to the preparation of hydrocarbons for the purpose of obtaining infra-red absorption spectra data.'[132] Some properties of the hydrocarbons obtained are given ; the spectra data are not recorded in this report. (2) 'The synthesis of some hydrocarbons'[133] i.e. paraffins, 4-methylindane, *iso*durene, and other alkyl benzenes. (3) 'Hydrocarbon syntheses'[134] i.e. heptanes, octanes, 2 : 3 : 5-trimethylhexanes and some decanes and cyclic compounds.

Recent advances in chemistry of hydrocarbons are reviewed by D. S. F. Birch.[135] Of the methods for producing *iso*-paraffins, the most important are isomerization and alkylation. Catalysts for isomerization and use of deuterium oxide in place of water and production of triptane by two different routes are described. Telomerization and the Oxo synthesis are briefly reviewed.

In a series of papers by H. W. Melville and J. C. Robb[136] on the kinetics of the interaction of atomic hydrogen with olefines a new type of reaction has been used for the removal of a hydrogen atom on a layer of molybdenum oxide or tungsten oxide. Data are given of the reactions of the type $H + C_nH_{2n} = C_nH_{2n+1}$. Olefines employed were ethylene, propylene, *iso*butane, *n*-pentene-2(*cis*) and 2 : 3 : 3-trimethylbutene-1. Tentative suggestions are put forward as to effect of structure on reactivity of the double bond, but a general figure for the collision efficiency of a hydrogen atom with an olefine appears to be between 10^{-3} and 10^{-4}.

Some results of the A.P.I. Project 6[137] are reported : the separation of the 177–200° C. fraction of the Ponca crude oil by distillation, azeotropic distillation and adsorption methods into an aromatic portion, a paraffinic plus *cyclo*-paraffinic portion and the isolation of pure *n*-undecane are described.

An important contribution to petroleum chemistry is reported by W. J. Zimmerscheid and his co-workers,[138] who show that urea forms solid and sufficiently stable complexes with linear aliphatic hydrocarbons for their separation from branched and cyclic hydrocarbons. This selectivity of urea, especially in conjunction with the older methods of separation, should make the technique of great value in research and processing of hydrocarbons.

Azeotrope formation between thiols and hydrocarbons has been studied by R. L. Denvers, F. A. Fidler and R. A. Lowry[139] covering 7 C_2, C_3 and C_4 thiols and 28 hydrocarbons. 55 azeotropes between thiols and paraffins and naphthenes are recorded. The correlations described have allowed the prediction of 17 azeotropes between these thiols and other hydrocarbons. Predictions have also been made for azeotropes between paraffins and straight-chain thiols such as methanethiol, 1-pentanethiol and 1-hexanethiol.

Jet and gas-turbine fuels

D. A. Howes and H. C. Rampton summarize[140] the information available on the properties of hydrocarbons boiling within the range 65–300° C. with particular reference to their use as constituents of fuels for gas-turbines. From the data presented in nine charts it is evident that the properties of hydrocarbons boiling in the range quoted, which are determined by chemical composition and structure, are closely interrelated, and that if the dicyclic and polycyclic hydrocarbons, not being major constitutents of such distillates, are ignored, the properties lie between tolerably well defined extremes set by the paraffins and aromatics respectively. Thus a fuel in this boiling range will have properties falling between these two extremes. These limits are tabulated.

In a paper on the effect of altitude conditions of fuels for aero-gas turbines, M. O'Farrell[141] gives the specification data for aviation gasoline, aviation kerosene, and two wide-range distillates: J.P.2 (AN–F–34), and J.P.3 (AN–F–58a); J.P.2 having a 2-lb./sq. in. max. Reid vapour pressure; J.P.3, having a 5-lb./sq. in. min. and 7-lb./sq. in. max. Reid vapour pressure. Data relating to air evolution, water and ice separation, fuel freezing, humidity effects and explosion risk are given and discussed with respect to the four fuels.

A combustion system for a 4800-h.p. gas turbine and the tests carried out on various fuels, including three grades of Bunker C fuel are described.[142] The data given include the liner temperatures, outlet gas temperatures, smoke and carbon formation. Ignition and operating patterns are shown and the factors which affect these features are discussed.

A jet fuel specification is given by C. R. Hudson of the Air Materiel Command, Dayton, Ohio,[143] as follows: A.P.I. gravity, 45–63; distillation, the temperature at 90% evaporated point shall not be less than 204·4° C., and the end point shall not exceed 316·5° C.; residue, not more than 1·5% and loss not greater than 1·5%; sulphur, not to exceed 0·5%; Reid vapour pressure, at least 5·0 lb./sq. in. but not more than 7 lb./sq.in.; gum, not to exceed 20 mg./100 ml.; aromatics, not to be more than 25%; bromine number, not more than 30·0; freezing point, not to be more than –60°C.; cal. val., not less than 18,400 B.Th.U./lb.

A new jet fuel (AN–F–58) has been developed for U.S. Army–Navy use which is basically a gasoline-type fuel with an octane number varying from 50–65. By changing the distillation process and blending the products, a higher percentage of usable jet fuel is obtained from any given quantity of crude oil.[144]

Gas oil and Diesel fuels

J. Mair, J. Sweetman and F. D. Rossini[145] report on the separation of the gas oil and wax fractions of petroleum by adsorption with silica gel. In a single-pass operation gas oil can be separated into three portions: a mixture of paraffins and naphthenes; a portion which is largely mononuclear aromatics; and a portion which is largely polynuclear aromatics. Similarly the wax fraction (aromatic-free but containing some oily constituents) can be separated into two portions: one which is largely paraffins and one which is largely naphthenes.

The separation of aromatic and saturate fractions in non-olefinic gas oils by adsorption on silica gel is described by T. Backhouse and A. J. Ham.[146] The relationship between composition, conventionally determined properties and ignition quality as defined by the cetane number were investigated. It is shown that in each series of blends of a particular gas oil and its saturate fraction there is a linear relationship between the cetane number and the percentage of saturates present. The various properties of the gas oils and their saturate fractions, e.g. Diesel index, percentage of carbon in the paraffinic structures and paraffin/naphthene ratio can be correlated with cetane number. Saturate fractions with lowest cetane numbers are predominantly naphthenic, and for all the saturate fractions, the ratio of the percentage of paraffins (n–d–M method) to cetane number is almost a constant.

Preliminary data as to the hydrocarbon types present in a Sinclair straight-run and a Stanolind cat-cracked Diesel oil are given by H. M. Smith (U.S. Bureau of Mines).[147] Investigations were made by silica-gel and distillation techniques. The straight-run oil contained about 80% paraffins and naphthenes, and the cat-cracked oil, about 60%. The ratios of paraffins to naphthenes are higher in the cracked stocks and *n*-paraffins are important components of both oils. There are indications of the presence of dicyclic naphthenes and fairly definite evidence of dicyclic and tricyclic aromatics; the aromatics in the cracked stock have a higher proportion of dicyclic and tricyclic compounds than occur in the straight-run material, and olefines play a minor role in both oils.

The fundamental physical chemistry of combustion of Diesel fuels is discussed by M. A. Elliott.[148] Combustion takes place in two stages: In the ignition delay stage a period of physical delay occurs, pending formation of a suitable fuel/air mixture, and a period of chemical delay during which pre-flame oxidation reactions leading to ignition, occur; during the inflammation stage extensive chemical reaction occurs and the potential energy of the fuel is released. The cetane number of a fuel is basically a measure of its chemical reactivity or chemical delay, but generalized correlations are not possible because of the effect of other variables such as volatility.

To augment the supply of Diesel fuels, wide-cut fuels are described.[149] One such cut, which gives a 43% yield against a 30% conventional yield, has been used in a locomotive over 15 months and has proved equal to the conventional cut. The wide-cut has a cetane number of 50; the specification is given.

Further information on the use of centrifuged boiler fuel in the Diesel

engines of the tanker 'Auricula' is recorded.[150] After three years' satisfactory operation on fuels of 1200 and 1500 sec. Redwood I at 100° F. with a saving of £7734 per annum, it is intended to use a fuel of viscosity as high as 3500 sec. Redwood I at 100° F.

The experience of a French shipping line in burning heavy fuel in Diesel-powered ships is discussed by J. Perrachon.[151]

Gelatin capsules containing basically an ethyl ether compound are described[152] for use in quick starting of gasoline or Diesel engines. They enable a Diesel engine to be started in less than 10 seconds at – 50° F.

Tests made to evaluate additives for improving cold starting characteristics of Diesel fuels are described.[153] With non-additive fuels an increase of 10 cetane numbers lowered permissible starting temperature about 12° F. Lowest starting temperature to be expected without starting aids was about 15° F. even when using premium grade kerosene. Of the various chemicals tested, none was effective in amounts less than 10%.

Details of the work carried out at Thornton Research Centre on Diesel fuels oils covering cold starting, knock, wear, fouling and exhaust smoke, are recorded by C. G. Williams and A. Wilson.[154]

B.P. 603,120 relates to the use of vanadium pentoxide deposited on the cylinder head, valve heads etc., of C.I. engines. It is stated that this material acts as an oxidation catalyst in the combustion of hydrocarbons, thus reducing the spontaneous ignition temperature and accelerating commencement of combustion.[155]

The causes of crankcase explosions were discussed by the Diesel Engine Users Association,[156] and they are reviewed also by R. McBrain,[157] who describes the spectroscopic examination of the ash from burned lubricating oil as a means of diagnosing defective working conditions and of forestalling such explosions and breakdowns.

The uses of Diesel fuel to disperse fog ('Fido') at Los Angeles Airport, U.S.A., and the installation, are described.[158] The consumption for full capacity is 1750 gal./min., the cost 75–80 dollars per landing of one plane.

The purpose and evolution of oil fuel specifications are discussed by C. W. G. Martin and D. R. Bailey,[159] and the special requirements for C.I. engine fuels and tests applicable are covered. Typical B.S. specifications for Diesel fuels are also given.

Furnace and boiler-fuel oils

Graphs comparing performance characteristics of different types of burners with straight-run and catalytically cracked fuels are discussed by B. R. Walsh.[160] With high-pressure gun burners, better combustion resulted when a large-orifice nozzle was employed. Of the types of turbulators tried with this type of burner, the four-bladed turbulator gave the best results.

Empirical relationships developed for computing volume of space required for oil fuel burning are given by R. Gibbs.[161] Explanatory examples show the dependence of combustion space on degree of atomization of the fuel.

A. S. C. Lawrence and W. Killner[162] discuss the factors causing stability of sea-water emulsions in fuel oil. The emulsifying agent was found to

be contained in the whole asphalt fraction of the oil. The mechanism of emulsion breaking by means of surface-active agents (e.g. Teepol 0·25%), which must be calculated on the water content of the emulsion, and by organic fluxing additives, is described.

H. J. Sharp and J. F. R. Ince describe[163] an investigation of the formation of deposits on the external surfaces of oil-fired boilers. They show the primary cause to be contamination of the fuel by sea-water. The emulsion process and properties of such emulsions and their breaking with Teepol are discussed.

A method of breaking emulsions is described[164]: five emulsions were rapidly and completely broken by the addition of a wetting agent under the conditions described, by the use of Teepol and Turkey red oil.

Lubricating oils and greases

An important research on the adhesive properties of lubricating oils is described by M. Freund.[165] In experiments with centrifugally driven discs of various metals, alloys, and polystyrene, made under controlled conditions, the film of oil adhering to the surface reaches a limiting value with increasing time of centrifuging, and is dependent only on the condition of the surface of disc and viscosity of the oil. It appears to be independent of the materials composing the disc and the chemical composition of the oil. It appears also, that for given conditions, equilibrium is always attained with a definite number of molecular layers in the film. Surface forces are apparently ineffective for the thicker oil films produced.

A. Marcelin[166] has measured the friction couple under boundary-layer conditions of oils of varying viscosity and under various loads. He found that friction is independent of load over the range 230–920 lb., but decreases slightly with increase in viscosity. Under hydrodynamic conditions, according to Newton's law, friction increases with increasing viscosity. The laws of friction for boundary lubrication therefore differ completely from those for either hydrodynamic or for imperfect lubrication (stratofilm). It is suggested that this is because in boundary lubrication the film is formed of molecules more or less polarized and firmly attached to the metal surface, the thickness of the film being a measure of the strength of this attachment. The law of friction in boundary lubrication, as a function of speed, has still to be determined.

L. Le Loup[167] shows that the critical limit between hydrodynamic and semi-fluid lubrication can be expressed in terms of $\frac{ZN}{p^{\frac{1}{2}}}$ rather than in terms of the well-known parameter $\frac{ZN}{p}$, where Z = viscosity of lubricant, N = journal speed, p = specific bearing load. Measurement of the coefficient of friction in the region of semi-fluid lubrication showed that for mineral oils it depends only on the value of the parameter $\frac{ZN}{p^{\frac{1}{2}}}$ for a given finish of the bearing surface. In this region of semi-fluid lubrication 'oiliness' properties of the lubricant come in to some extent; however, more effect can be expected from a better finish of the surfaces.

Measurements of kinetic boundary friction are discussed, in relation

to their utility in characterizing the 'oiliness' of a lubricant, by F. T. Barwell and A. A. Milne.[168] It is shown that 'oiliness' is not a unique property of a lubricant, but that friction varies widely with such factors as speed of sliding, roughness and hardness of surfaces and temperatures.

The anti-seizure properties of boundary lubricants are described by R. E. Thorp and R. G. Larsen.[169] The study of boundary lubrication, particularly the nature of anti-seizure protection, was made in modifications of the four-ball apparatus by observing the variation, with sliding velocity, of the coefficient of friction and contact resistance. The friction of effective boundary lubricants is independent of the sliding velocity in the low speed range (0·1 to maximum of 8 cm./sec.), or decreases very slightly as speed approaches zero. On the other hand, poor boundary lubricants are those not containing polar constituents or, to a lesser degree, those containing polar molecules capable of physical adsorption only; they are characterized by relatively high friction, often increasing at low sliding velocities to values characteristic of unlubricated surfaces. The actual magnitude of the coefficient of friction under non-seizing conditions is determined largely by the adsorbed film thickness which can be maintained between the rubbing surfaces.

Discussing the graphoid surface in lubrication, E. A. Smith[170] states that an *X*-ray pattern for stearic acid on steel shows that the polar molecules are not fully oriented. When stearic acid is added after the formation of a graphite film on the metal, the pattern shows a rapid orientation of the polar groups.

Technical Note No. 1845,[171] Stanford University, U.S.A., reports the suppressing of foam in an aircraft lubricating-oil by re-cycling it through a column of activated charcoal at 50° c. After this treatment, the oil at 100° c. produced only one-tenth the volume of foam given by the untreated oil. Porocel, activated magnesium oxide and silica gel were not so effective.

Dialkyl selenides[172] are shown to be far more effective oxidation inhibitors than the corresponding sulphides. The selenium oxide formed in the reaction is thermally decomposed to yield the original selenide in appreciable percentage; thus a partial regenerative mechanism is operating.

Complex thiophosphoric amides as lubricant additives are described by J. D. Bartleson and M. C. Sunday.[173] Tests are described of a typidal product from barium hydroxide, phosphorus pentasulphide and dioctadecylamine which show the product to be effective as a detergent, pour-point depressant, corrosion inhibitor and viscosity-index (V.I.) improver.

The use of polymethacrylates as V.I. improvers and pour-point depressants is described by W. L. Van Horne.[174]

New heavy-duty motor oils are described,[175] composed of conventionally refined petroleum fractions containing 8–12% and 16–20% additive, as compared with 4–6% in lubricants meeting U.S. Army Ordnance Specification 2–104B. The additives consist of oxidation inhibitors and specific compounds to neutralize corrosive products of combustion. These lubricants reduce the wear that occurs from the use of high-sulphur fuels in Diesel engines.

Additive treated crankcase lubricants are discussed by C. F. Prutton.[176] Detergents containing calcium, barium or aluminium, although satisfactory

with babbitt bearings were unsatisfactory with copper–lead and certain other alloy bearings. Early corrosion additives did not protect copper–lead and cadmium–lead. Modern detergent additives derived from a phenol, a sulphonic or phosphoric acid and containing a metal are described. A suggested mechanism for their action is presented, but the chief action of a sulphonate is physical, namely the absorption of varnish-forming substances before they can build up deposits. A possible mechanism of the effective action of corrosion inhibitors is postulated.

The factors influencing upper-cylinder deposition phenomena have been investigated by H. Diamond, H. C. Kennedy and R. G. Larsen.[177] They used a motor-driven Lauson engine with the jacket heated by circulating hot oil, the ignition and fuel system and valves being completely removed. It is shown that deposits can be formed solely by the oxidation of the lubricating oil, that pre-oxidation of the oil at moderate temperature affects its subsequent behaviour at high temperatures, and that only sulphur dioxide promotes, to any degree, the formation of deposits.

F. F. Farley and R. J. Greenshields[178] report that low engine-jacket temperatures promote sludge and lacquer formation. Incomplete combustion products during low-temperature operation result in deposits which pass the piston as blow-by, condense on cylinder walls and flow into the crankcase. Lacquer on the pistons and sludge particles in the circulating oil are formed from the oxidation and polymerization of the products during re-circulation of crankcase oil. Agglomeration and coagulation of the sludge particles then occur in the cooler parts of the engine.

C. W. Georgi[179] shows that the properties of motor oils which have the greatest effect on consumption tendency are volatility, viscosity and viscosity-index, but their interdependence makes individual evaluation difficult. Oils with low volatility (within defined limits), high viscosity and high V.I. tend to possess the lowest consumption characteristics. Viscosity-index improvers do not alter oil consumption appreciably from that of petroleum-base oils alone. Oils containing V.I. improvers are non-Newtonian fluids and their viscosity and V.I. determinations, as conventionally made, apply only at very low shear-rates and may be very misleading in terms of the very high shear-rates developed in engines.

The behaviour of typical turbine oils under oxidation has been observed by D. Wyllie and G. C. N. Cheesman.[180] Under the conditions of the I.P. test 114/47, conventionally refined turbine oils yield only negligible quantities of peroxide while oxidation is in progress, but a marked rise in peroxide value of the oil takes place at the conclusion of the high temperature oxidation. This can be explained by assuming that peroxide formation and destruction take place at different relative rates during and after the oxidation, although the oxidized oil is susceptible to peroxide formation at room temperature.

The oxidation test of Pope and Hall is not considered a suitable corrosion test for turbine oils, and the use of interfacial tension as a measure of oxidation is not advised. Results of I.P. test 114/47 on four pre-selective gear-box oils gave reasonable correlation between laboratory results and service experience.

S. A. McKee *et al.*[181] describe an unusual application of the S.A.E. E–P

lubricant testing machine for the determination of the wear with gear lubricants under conditions emulating high torque and low speed. The results of tests indicate that the method of operating this machine provides a sensitive measure of rate of wear obtained. Information is given on the run-in wear, the change in surface roughness of the test cups with wear and the effect of the original surface roughness on the rate of wear.

J. Tadayon and E. W. Hardiman and A. H. Nissan[182] present a nomogram from which the 'rational viscosity index' may be determined. The values may be converted into Dean and Davis V.I. by the equation V.I. = $(60 - \text{antilog } n)\ 3{\cdot}63$ or directly from the curve representing V.I. as a function of n which is included in the nomogram.

J. E. Champion describes[183] tests carried out on an A–65 Continental, 4-cylinder engine to investigate ring-sticking. Twenty mineral-base and compounded oils with additives were examined. Ring-sticking was indicated by the increase in crankcase pressure.

A short note discusses[184] the use of radio-isotopes in the oil industry, covering their employment in pipe-line-batching, liquid-level measurement, measurement of wall thickness, engine-wear testing; their safe handling is discussed. The cost of radioactivated cobalt for the purpose is $50 per g.

A new method of measuring bearing wear is described.[185] A pump is being tested which has one of the big end bearings fitted with a cast-iron bush, which has been made radioactive so that it emits β-rays; any particles worn off the bush are taken up by the oil. The oil is collected and placed in a rotating drum with strips of photographic film; radiations from the particles cause fogging of the film, and the density of the fogging is proportional to the radioactive content of the oil. It is possible to calculate the bearing wear over a given period to amounts as small as 1 μin.

A similar method is described[186] in which the piston rings are irradiated and the amount of radioactive metal in the oil is determined by a Geiger counter.

A laboratory beaker-test is described[187] for evaluating the corrosive potentialities of lubricating oils towards cadmium–nickel bearings. The method yields repeatable results which appear to give satisfactory correlation with the Hercules engine tests.

S. G. Daniel[188] describes the construction and operation of a viscometer to measure the viscosity at shearing stresses up to 45,000 dynes/cm^2. at temperatures from 20 to $-25°$ c., and gives results obtained from the examination of the viscous behaviour of aero-engine lubricants at low temperatures.

From *X*-ray diffraction patterns and differential heating curves of numerous samples of aluminium, barium, calcium, lithium, sodium and mixed-base greases, and for the corresponding oil-free soaps, Vold *et al.*[189] show that the structure of the crystallites may be modified by *in situ* formation; it is different from that obtained when prepared in the oil-free state. The nature and extent of such effects vary with the soap cation and with the incorporation of additives. On heating, the greases undergo thermal transformations which are in some cases closely related to the polymorphic transformations of the oil-free soaps. In other cases there

exist more complex solubility relations involving swelling of the soap to form liquid crystalline solutions of oil in soap.

Hypermatic,[190] a new self-feeding grease recently announced in America, is claimed to be compressible to about 50% of its atmospheric volume at 300 to 500 lb./sq. in. and is said to be stable up to 300° F. for a considerable time. It is self-feeding by virtue of the energy stored in it while under pressure in the lubricant reservoir of the valve. It is thought to be a stabilized gas–liquid emulsion.

An empirical equation[191] is given for the more rapid calculation of pressure-flow relations in non-Newtonian fluids; it takes into consideration the thixotropic change in the flowing material.

The solubility relations of metal soaps in hydrocarbons are represented by phase diagrams. The aspects considered include experimental methods for phase studies, phase behaviour of anhydrous soaps in hydrocarbons, effect of additives, and relations between phase behaviour and grease properties.[192]

C. J. Boner[193] in a series of papers on the manufacture of lubricating greases, describes fully the processes and the materials used, including additives for the many different types of grease, and describes their properties.

Wax, petrolatum, etc.

A simple method of demonstrating the thixotropic behaviour of petroleum jelly is described by A. de Waele.[194] The behaviour to polarized light of the sheared and unsheared sample is indicated and the results of a few qualitative observations on a sample of petroleum jelly which had been treated in various ways are recorded. In a second note[195] on the subject, more precise observations on the reversible change of consistency brought about by low and fast shear on the jelly, are recorded.

A description is given of the behaviour of some binary mixtures of hydrocarbons is given by W. M. Mazee[196] in a paper on the properties of paraffin wax in the solid state. It was found that a mixture of n-$C_{21}H_{44}$ and n-$C_{23}H_{48}$ forms a continuous series of mixed crystals, whereas n-$C_{21}H_{44}$ and n-$C_{31}H_{64}$ forms an eutectic, so that n-$C_{21}H_{44}$ and n-$C_{31}H_{64}$ crystallize separately. A mixture of n-$C_{24}H_{50}$ and 13-methylpentacosane also gave a binary system with an eutectic. On the strength of these phenomena a hypothesis was formulated for the structure of commercial paraffin waxes.

A. Kinsel and J. Phillips[197] describe a method for the measurement of gloss of petrolatum or paraffin waxes. The lustre index is defined and experimental data are given. The lustre index is quite independent of the colour and viscosity (at 210° C.) of the sample; the softer samples, and the samples with the lower melting points, tend to have the higher lustre indexes, the petroleum waxes, whether micro- or macro-crystalline, all have approximately the same lustre index.

A fundamental approach to the problem of propane de-waxing has been made[198] through microscopic studies of wax crystals from a Mid-Continent paraffin distillate. Crystal formation is described and shown by photographs. The influence of small and large amounts of asphalt on crystal formation is described. When no de-waxing aid (asphalt) was present

the crystals were in the form of plates arranged in a flat or honeycomb structure. When a small amount of asphalt was present the wax crystallized rapidly, immediately below the crystal point, into spherical particles. On further chilling each nucleus was surrounded by a shell of radiating needles. With large amounts of asphalt numerous small nuclei formed at the crystal point and grew until the filtering temperature was reached. No surrounding shell of radiating needles appeared with these formations.

In 'The effect of oil on plastic properties of petroleum waxes,' W. L. Nelson and L. D. Stewart[199] describe equipment and procedure for a flexibility test in which 'a stick of wax is bent through a 60° angle until rupture occurs.' They state that compressive strength is more dependable than tensile strength tests. Oil appears to enter the space between the interlocking crystals altering the structure only by dissolving some of the wax, whereas oil enters and dilutes the continuous phase of the microcrystalline waxes gradually altering the properties of the wax and possibly precipitating additional micro-crystals. Only with extremely hard or high melting point microcrystalline waxes does oil improve the plasticity or flexibility of a wax.

Asphaltic bitumen

Two methods for improving the adhesion of bitumen to road aggregates are described[200]: treatment of the bitumen, and treatment of the aggregate. It is stated that chemical additions to the bitumen were more efficient than the treatment of the aggregate; amine hydrochlorides were the most effective of the additives studied for this purpose. Treatment of the aggregate with cupric chloride and Emulsol-5049W (amine hydrochlorides) gave excellent affinity for the bitumen, but other mixtures of amine chlorides or amine salts were less effective.

Coloured asphalts[201] have been shown by the Road Research Laboratory to be producible by the use of a resinous binder known as 'Cados.' By using white calcined flint with the binder a fine white asphalt is obtained. The addition of 4% of titanium oxide imparts a creamy colour to the product. Effective red, green, blue and yellow asphalts can be made by the addition of only about 2% of pigment. The cost is not much greater than for ordinary asphalt.

In 'Some cold bituminous constructions' L. G. Gabriel describes[202] the use of bituminous emulsions: in the 'Coldprovia' process a final road binder is produced by the interaction actually, within the road carpet, of an oil and a hard bitumen which, in the proportions employed will eventually produce a finished bitumen of the desire characteristics; in the 'retread' process suitable salvaged material is used; in soil stabilization for the construction of a road base the bituminous stabilizer serves to maintain the bearing capacity of the soil by minimizing the ingress of water into the sub-base; the 'earth mix' process is a method of incorporating stable emulsion into sub-soils of suitable grading to give light traffic surfaces for farm roads etc. He also outlines other uses for emulsions, e.g. to conserve warmth and moisture in the soil. The Shell-perm and Cretolas processes are outlined.

H. Eilers,[203] in a paper on the colliodal structure of asphalt, records the

solubility and composition of the asphaltenes and their voluminosity in solutions. He correlates the various deformation schemes illustrated with the structure of the asphalts, i.e. the purely viscous, the viscous with elastic effect (sol type) and the yield value with elastic effect and breakdown of structure (gel type).

Further investigations of the surface-tension rule for asphaltic bitumen described by Nellensteyn and Lohman in 1928 are recorded.[204] Organic liquids are shown to be divided into solvents and flocculating agents, according to their surface tension, i.e. those above 26 dynes/cm., and those below 24 dynes/cm.; the former are aromatic compounds and the latter are aliphatic in character.

Special products

An extensive review of the petro-chemical industry in South-West U.S.A. is given by W. F. Bland.[205] It describes the many company activities, the investment in them compared with that in the chemical industry, the present status, locations and the raw petroleum products employed. The chemicals produced by the individual companies are described in detail and future extensions are discussed. The following compounds, among many listed, indicate the wide range of chemicals produced: acetic anhydride, *iso*propanol, vinyl acetate, vinyl chloride, ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, *n*-butylaldehyde, propionaldehyde, methyl propyl ketone, *iso*butyl ketone, perchloroethylene, perchloroethane, hexachloroethane, ethylene oxide, epichlorohydrin, methyl *iso*butyl ketone and carbinol, acrolein and mesityl oxide.

The American position in the petro-chemical field is reviewed by R. F. Goldstein.[206] New products and processes discussed include: hypersorption, Oxo process, alkane sulphonic acids, propiolactone, cresol, methylstryene, cumene, hydroperoxide, thiophen derivatives, nylon and orlon.

Chemicals from the hydrocarbon synthesis are described by T. Q. Eliot *et al.*[207] The catalyst, pressure and temperature used and distribution of hydrocarbons/chemicals are shown in comparison with data from the Synol, Synthine and Methanol processes. Separation problems of the water-soluble and oil-soluble types are discussed. Azeotropes of some of the chemicals are given.

P. W. Sherwood describes[208] the reactions and limitations of dehydration methods for the manufacture of primary long-chain alcohols and the preferred processes for their production, viz., the Synol and Oxo methods. The former has not so far attained industrial significance. The Oxo process, for the synthesis of isomeric alcohols of high molecular weight, is being operated by the Esso Company at Baton Rouge for the manufacture of *iso*-octyl alcohol from a selected olefine fraction and water-gas.

The Oxo process is used on a pilot plant scale by Rohm and Haas at Bridesburg, Pa., for producing nonanoic acid, nonylamine, nonyl aldehyde, cyanohydrin, α-hydroxydecanoic acid, octadecanyl aldehyde and its alcohol.

The purification of natural gas to ensure delivery of a product with a cal. val. of 1000 B.Th.U. in the Santa Maria district, California, is

described.[209] The carbon dioxide recovered after dehydration, cooling, compression and liquefaction is converted into the solid product. Three presses produce 60 tons per day of 'dry ice' for marketing.

The sources of colour of commercial naphthenic acids have been investigated.[210] Efficient fractionation does not completely remove either the organic source of the colour or the oil associated with the acid. It appears that the naphthenic acid molecule is degraded by heat and/or oxidation, producing products of darker colour than the original, and that the darkening of commercial acids under manufacturing conditions is a phenomenon related to the acids themselves as well as to the accompanying oil.

Analysis and testing

H. R. Linden in 'The relationship of physical properties and ultimate analysis for liquid hydrocarbons'[211] shows that apparently unrelated properties of hydrocarbons, e.g. heat of formation, heat of combustion, specific heat and maximum flame temperature are all functions of the C/H ratio. A criterion based on simple physical tests which correlates with the determination of C/H ratio is presented.

H. C. Rampton[212] describes a method of hydrocarbon-type analysis for cracked gasolines etc. which permits the determination of the aromatics, naphthenes, paraffins, alkenes and cyclenes, with an accuracy of 0·15, 0·65, 0·35, 0·95 and 0·75% respectively; typical analyses are recorded. The proposed method cannot be considered as a substitute for any existing standard inspection procedures, since the data are obtained in detail. The time taken is 200 man-hours.

An ignition delay meter for the determination of cetane number is described.[213] It overcomes previous difficulties and possesses numerous advantages over other methods of measurement. Commencement of injection and combustion can be detected and the ignition delay can be measured even under accelerating conditions.

Two lubricating-oil testing engines have been described in articles covering their development, design and construction, special features, and performance. Both have been designed in collaboration with the Institute of Petroleum 'Tests of Lubricants Panel.' They are: (i) The Anglo-Iranian company's engine,[214] for spark-ignition engine lubricating oil testing, for replacing the ring-gumming-R.G.-2, aviation lubricating-oil test; (ii) the Ricardo–Shell engine,[215] a compression-ignition engine for testing Diesel lubricating oils. This engine should enable the full procedure of the CRC-1 test series to be completed in about one-third of the time normally taken.

Functional tests for lubricating oils and their interpretation are described.[216] These tests bridge the gap between conventional and actual service tests and give information on the actual quality of a lubricant. An example of one such test is given involving an apparatus for evaluating hydraulic oils. It consists of a vane-type pump through which the oil is circulated. New parts are fitted for every test, after which the vanes are tested for loss in weight and the whole system is examined for corrosion and deposits. The conditions for successful functional tests are enumerated and data for two oils and their interpretation are given.

A test procedure is described[217] for establishing the performance of oils under low-temperature fluid conditions. This flow-resistance test appears to be a superior method of evaluating the low-temperature flow characteristics of a winter-type motor oil. A 10-W motor oil should have a maximum natural pour-point of 15° F., a maximum S.U. viscosity of 190 sec. at 100° F. and V.I. above 100 in order to obtain a flow resistance below 30 sec.

A thrust-bearing apparatus adaptable to the Sohio oxidation test for lubricating oils is described.[218] Operating conditions and catalyst components have been determined so that a 10-hr. test correlates with the 36-hr., L-4 Chevrolet A.S.T.M. test for varied groups of inhibited oils. At the same time correlative information is obtained of the oxidation characteristics of the oils.

Recent developments[219] in the procedure for conducting the immersion-compression test are recorded and additional results of its application to studies of various factors affecting the resistance of bituminous aggregates to the action of moisture are given. By this test a quantitative index of damage caused by moisture is provided by the comparison of the compressive strengths of laterally unsupported moulded cylinders with those of duplicate specimens after immersion in water for a definite time. Tendency to strip is indicated by reduction in strength caused by loss in adhesion of bituminous film to aggregate particles.

References

[1] Duff, D. E., *Oil Gas J.*, 1949, **48**, No. 33, 170, 171, 180
[2] Ibid., **47**, No. 43, 98
[3] *Petrol. Times*, 1949, **53**, 172
[4] *Oil Gas J.*, 1949, **47**, No. 38, 84
[5] Ibid., No. 35, 159
[6] Ibid., 263
[7] *Petroleum, Lond.*, 1949, **12**, 191
[8] *Oil Gas J.*, 1949, **48**, No. 7, 219
[9] Ibid., **47**, No. 51, 140
[10] Ibid., 138
[11] *J. Inst. Petrol.*, 1949, **35**, 309
[12] *Oil Gas J.*, 1949, **48**, No. 12, 238
[13] Ibid., No. 4, 70
[14] Ibid., No. 53, 94
[15] *Rev. dei Combust.*, 1949, **111**, 189
[16] *Nat. Petrol. News*, 1949, **41**, No. 37, 20, 40
[17] *Petrol. Times*, 1949, **53**, 831
[18] *Petrol. Refin.*, 1948, **27**, No. 9, 358; *Oil Gas J.*, 1949, **47**, No. 47, 248
[19] Bruner, F. H., *Ind. Eng. Chem.*, 1949, **41**, 2511
[20] Clark, E. L., Kallenberger, R. H., Browne, R. Y. and Phillips, J. R., *Chem. Engng. Prog.*, 1949, **45**, 651
[21] Pichler, H. and Ziesecke, K. H., *Brennstoff Chem.*, 1949, **20** (1/2), 13
[22] Clark, A., Andrews, A. and Flemming, H. W., *Ind. Eng. Chem.*, 1949, **41**, 1527
[23] Ball, J. S., Dinneen, G. W., Smith, J. R., Bailey, C. W. and Van Meter, R., ibid., 581
[24] Tuttle, R. B., *Oil Gas J.*, 1949, **47**, No. 39, 201
[25] Idem, ibid., **48**, No. 12, 208
[26] Ibid., 1949, **48**, No. 33, 197
[27] *Petrol. Times*, 1949, **53**, 364
[28] *Oil Gas J.*, 1949, **47**, No. 47, 153
[29] *Petrol. Times*, 1949, **53**, 199, 662
[30] *Refiner*, 1949, **28**, No. 4, 130; *Chem. & Ind.*, **1949**, 459

[31] *Refiner*, 1949, **28**, No. 9, 148
[32] *Petrol. Times*, 1949, **53**, 997
[33] *Industr. Chem. chem. Mfr*, 1949, **25**, 392.
[34] *Petrol. Times*, 1949, **53**, 816
[35] Ibid., 135 ; *Chem. Tr. J.*, 1949, **124**, 186
[36] *Chem. Tr. J.*, 1949, **124**, 186
[37] *Inst. Petrol. Rev.*, 1949, **3**, 175
[38] Sutherland, R. E. and Dougey, J. L., *Petrol. Processing*, 1949, **4**, 679
[39] Holt, B. M., ibid., 681
[40] Feuchter, C. F., *Oil Gas J.*, 1949, **48**, No. 11, 62
[41] Griswold, J. and Morris, J. W., *Ind. Eng. Chem.*, 1949, **41**, 331
[42] Griswold, J. and Walkey, J. E., ibid., 621
[43] Kuo-tsung Yu and Coull, J., *J. Inst. Petrol.*, 1949, **35**, 770
[44] Scheibel, E. G., *Chem. Engng. Progress*, 1948, **44**, 927
[45] Garner, F. H., *Ind. Chem. chem. Mfr*, 1949, **25**, 238
[46] Marschner, R. F. and Croppor, W. P., *Ind. Eng. Chem.*, 1949, **41**, 1357
[47] *Analyt. Chem.*, 1949, **21**, 831
[48] *Chem. Engng. Progr.*, 1949, **44**, 905
[49] *Oil Gas J.*, 1948, **47**, No. 7, 71
[50] Cole, R. E. and Davidson, D. D., *Ind. Eng. Chem.*, 1949, **41**, 2711
[51] Lien, A. P., McCaulay, D. A. and Evering, D. L., ibid., 2698
[52] *Petrol. Processing*, 1949, **4**, 27, 153, 258, 401, 530, 667, 893
[53] Ibid., 519
[54] Ibid., 395
[55] *Oil Gas J.*, 1949, **48**, No. 16, 101
[56] Ibid., 1948, **47**, No. 29, 95
[57] *Petrol. Refin.*, 1949, **28**, No. 5, 117
[58] Berg, C., Fairfield, R. G., Imhoff, D. H. and Hulter, H. J., *Oil Gas J.*, No. 52, 1949, **47**, 95
[59] Goldblatt, S. and Kelly, H. M., ibid., **48**, No. 21, 54
[60] *Petrol. Refin.*, 1949, **28**, No. 4, 171
[61] Ruhemann, M. and Steiner, H., *Chem. Engng. Process Industr.*, 1949, **30**, 314
[62] Eagle, S. and Scott, J. W., *Petrol. Processing*, 1949, **4**, 881
[63] *Ind. Eng. Chem.*, 1949, **41**, 417
[64] *Petrol. Processing*, 1949, **4**, 660
[65] *Petrol. Refin.*, 1949, **28**, No. 4, 111
[66] *Petrol. Processing*, 1948, **3**, 1169 ; 1949, **4**, 32, 145, 254, 415
[67] Bowman, J. R. and Burk, H. S., *Ind. Eng. Chem.*, 1949, **41**, 2008
[68] *Inst. Petrol. Rev.*, 1949, **3**, 107
[69] *Oil Gas J.*, 1949, **47**, No. 37, 89
[70] Schutte, S. H. and Rose, K. E., *Petrol. Engng.*, 1949, **21**, No. 5, C–7
[71] *Oil Gas J.*, 1949, **48**, No. 10, 90
[72] *Petrol. Times*, 1949, **53**, 386
[73] Walker, R. and Applebee, H. C., *Gas Times*, 1949, **61**, 240
[74] Berti, V., Salvi, G. and Chisoni, V., *Rev. dei Combust.*, 1947, **1**, 129
[75] Conn, A. L. and Brackin, C. W., *Ind. Eng. Chem.*, 1949, **41**, 1717
[76] *Oil Gas J.*, 1949, **47**, No. 37, 78 ; *Petrol. Refin.*, 1949, **28**, No. 1, 110
[77] Hornaday, G. F., Noll, H. D. Peavy, C. C. and Weinrich, W., *Oil Gas J.*, 1949, **47**, No. 49, 90
[78] *Petrol. Engng.*, 1949, **21**, No. 8, C–22
[79] *Oil Gas J.*, 1949, **47**, No. 47, 218
[80] Ibid., No. 49, 95
[81] Steffens, J. H., Zimmerman, M. W. and Laituri, M. J.; *Chem. Engng. Progr.*, 1949, **45**, 269
[82] *Oil Gas J.*, 1949, **48**, No. 14, 74
[83] *Petrol. Engng.*, 1949, **21**, No. 8, C–16
[84] *Petrol. Processing*, 1949, **4**, 409
[85] Weil, H. B., ibid., 547
[86] *Proc. roy. Soc.*, 1949 [A], **196**, 105
[87] *Rev. Inst. franç. Petrole*, 1949, **4**, 166, 207
[88] *J. Inst. Petrol.*, 1949, **35**, 118
[89] *Ind. Eng. Chem.*, 1949, **41**, 182

[90] *J. Inst. Fuel*, 1949, **22**, 150
[91] *Fuel, Lond.*, 1949, **28**, 2
[92] Ibid., 145
[93] Powling, J., ibid., 25
[94] *Nature*, 1949, **163**, 883
[95] Zaharov, B. A. and Nicolaev, T. H., *J. tech. Sciences, USSR*, 1948, No. 1, 79
[96] I.Ae.S. Preprint, No. 222, March 18, 1949
[97] *Ind. Eng. Chem.*, 1949, **41**, 1851
[98] *Fuel, Lond.*, 1949, **28**, 121, 200, 205, 225, 228
[99] *Nature*, 1949, **164**, 708
[100] *Soc. auto. Engrs. J.*, 1949, **57**, 64
[101] *Motor Ship*, 1949, **30**, 362
[102] Ridley, C., *Auto. Engr.*, 1949, **39**, 21
[103] *Ind. Eng. Chem.*, 1949, **41**, 897
[104] Livingston, H. K., *Oil Gas J.*, 1949, **47**, No. 38, 67
[105] Banks, F. R., *J. Inst. Petrol.*, 1949, **35**, 264
[106] *Auto. Engr.*, 1949, **39**, 304
[107] Rosenwald, R. H. and Hoatson, J. R., *Ind. Eng. Chem.*, 1949, **41**, 914
[108] Ibid., 918
[109] Ibid., 924
[110] Ibid., 2715
[111] Ibid., 907
[112] Ibid., 1723
[113] Van Hartesvelt, C. H., *Soc. auto. Engrs. Quart. Trans.*, 1949, **3**, 277
[114] Padovani, C., Berti, V. and Leidi, G., *Rev. dei Combust.*, 1948, **2**, 265
[115] Miller, C. D., Olsen, H. L., Logan, W. D. and Osterstrom, G. E., N.A.C.A. Report, No. 857, *Aircr. Engng.*, 1949, **21**, 262
[116] *Soc. auto. Engrs. Quart. Trans.*, 1948, **2**, 532
[117] *Oil Gas J.*, 1949, **48**, No. 18, 71
[118] Watson, F. R., Caudel, F. H. and Heldman, J. D., Soc. Auto. Engs. Preprint No. 265, Nov. 4–5, 1948
[119] *Auto. Industr.*, 1949, **101**, 28, 34, 36
[120] *A.S.T.M. Bull.*, 1949, No. 156, 56
[121] *Auto. Engrs.*, 1949, **35**, 246
[122] *Canad. J. Res.*, 1949 [F], **27**, 307
[123] *Nature*, 1949, **162**, 893
[124] Ibid., **163**, 370
[125] *Canad. J. Res.*, 1949 [F], **27**, 211
[126] *Ind. Eng. Chem.*, 1949, **41**, 893
[127] *Trans. Faraday Soc.*, 1949, **15**, 1043
[128] *Soc. auto. Engrs. Quart. Trans.*, 1949, **3**, 306
[129] Shackleton, L. R. B., *Industr. Chem. chem. Mfr*, 1949, **25**, 423
[130] *Nature*, 1949, **163**, 665
[131] *Canad. J. Res.*, 1949 [A], **27**, 151
[132] Jamison, M. M., Lesslie, M. S. and Turner, E. E., *J. Inst. Petrol.*, 1949, **35**, 590
[133] Hickinbottom, W. J. and Porter, C. R., ibid., 621
[134] Buck, F. R., Elsner, B. B., Henshall, T., Moore, T. S., Murray, A. R., Morrell, S. H., Muller, G., Plant, M. M. T., Smith, J. C. and Wallsgrove, E. R., ibid., 631
[135] *Nature*, 1949, **163**, 272
[136] *Proc. roy. Soc.*, 1949 [A], **196**, 445, 466, 479, 494
[137] Epstein, M. B., Mair, B. J., Willingham, C. B. and Rossini, F. D., *J. Res. nat. Bur. Stand.*, 1949, **42**, 139
[138] Zimmerschied, W. J., Dinerstein, R. A., Weitkamp, A. W. and Marescher, R. F., Adsorption Symposium, A.C.S. Atlantic City meeting, Sep., 1949
[139] *Ind. Eng. Chem.*, 1949, **41**, 2727
[140] *J. Inst. Petrol.*, 1949, **35**, 419
[141] *Shell Aviation News*, 1949, No. 135, 16
[142] Buckland, B. O. and Berkey, D. C., A.S.M.E. Paper, No. 48–A–109, Nov. 28–Dec. 3, 1948
[143] *Nat. Petrol. News*, 1949, **41**, No. 14, 19
[144] *Oil Gas J.*, 1949, **47**, No. 46, 194
[145] *Ind. Eng. Chem.*, 1949, **41**, 2224

[146] *Fuel, Lond.*, 1949, **28**, 246
[147] *Soc. auto. Engrs. Trans.*, 1949, **3**, 164
[148] Ibid., 490
[149] Crampton, A. B., Hulse, S. H. and Rickles, N. H., *Soc. auto. Eng. J.*, 1949, **57**, 34; *Petrol. Processing*, 1949, **4**, 131
[150] *Petrol. Times*, 1949, **53**, 772
[151] *Motor Ship*, 1949, **30**, 147
[152] *Oil Gas J.*, 1949, **47**, No. 39, 353
[153] *Auto. Engr.*, 1949, **39**, 264
[154] *Mech. World*, 1948, **124**, 558
[155] *Commerc. Motor*, 1948, **88**, 510
[156] *Gas Oil Pwr.*, 1949, **44**, 35
[157] *Diesel Railway Traction*, July, 1949, p. 134
[158] Beadle, W. N. and Bensuen, M. D., *Oil Forum*, 1949, **3**, 60; *Nat. Petrol. News*, 1949, **41**, No. 24, 18
[159] *Inst. Petrol. Rev.*, 1949, **3**, 213
[160] *Fuel Oil, Oil Heat.*, 1949, **7**, 54
[161] *Chem. Engng.*, 1949, **56**, No. 1, 112
[162] *J. Inst. Petrol.*, 1948, **34**, 821
[163] *Engineering*, 1949, **167**, 361
[164] Lawrence, A. S. C., Barby, D. and Mills, O. S., *Nature*, 1949, **164**, 536
[165] *Petroleum, Lond.*, 1949, **12**, 29
[166] *C.R. Acad. Sci., Paris*, 1949, Feb., 650
[167] *Rev. gén. Méchanique*, 1949, **33**, 34, 81
[168] *J. Inst. Petrol.*, 1949, **35**, 455
[169] *Ind. Eng. Chem.*, 1949, **41**, 938
[170] *Petroleum, Lond.*, 1949, **12**, 84
[171] *Chem. Age*, 1949, **61**, 47
[172] Denison, G. H. and Condit, P. C., *Ind. Eng. Chem.*, 1949, **41**, 944
[173] Ibid., 948
[174] Ibid., 952
[175] Guthrie, V. B., *Petrol. Processing*, 1949, **4**, 981
[176] *Soc. Auto. Engrs J.*, 1949, **57**, 30
[177] *Ind. Eng. Chem.*, 1949, **41**, 495
[178] Ibid., 902
[179] *Petrol. Refin.*, 1949, **28**, No. 1, 98; *Soc. Auto. Engrs. Trans.*, 1949, **3**, 431
[180] *J. Inst. Petrol.*, 1949, **35**, 61
[181] McKee, S. A., Swindells, J. F., White, H. S. and Mountjoy, W., *J. Res. nat. Bur. Stand.*, 1949, **42**, 125
[182] *J. Inst. Petrol*, 1949, **35**, 28
[183] *Soc. Auto. Engrs. J.*, 1949, **57**, 40
[184] *Oil Gas J.*, 1949, **48**, No. 31, 42
[185] *Engineering*, 1949, **168**, 9
[186] Pinotti, P. L., Hull, D. E. and McLaughlin, E. J., *Petrol. Engng.*, 1949, **21**, No. 6, C–5
[187] Matthews, F. H. W., *J. Inst. Petrol.*, 1949, **35**, 436
[188] Ibid., 1949, **35**, 516
[189] Void, M. J., Hattiangdi, G. S. and Vold, R. D., *Ind. Eng. Chem.*, 1949, **41**, 2539
[190] *Chem. Industr.*, 1949, **65**, 496
[191] Wilson, J. W. and Smith, G. H., *Ind. Eng. Chem.*, 1949, **41**, 770
[192] Vold, M. J. and Vold, R. D., *Institute Spokesman*, 1949, **13**, 10
[193] *Petrol. Refin.*, 1949, **28**, No. 3, 109; No. 4, 127; No. 5, 129; No. 6, 152; No. 7, 164
[194] *Nature*, 1949, **163**, 248
[195] Ibid., 774
[196] *J. Inst. Petrol.*, 1949, **35**, 97
[197] *Petrol. Refin.*, 1949, **28**, No. 4, 147
[198] Chamberlain, N. F., Dinwiddie, J. A. and Franklin, J. L., *Ind. Eng. Chem.*, 1949, **41**, 566
[199] Ibid., 2231
[200] Snyder, M. J. and Pavlish, A. E., ibid., 2649
[201] *Petroleum, Lond.*, 1949, **12**, 267
[202] *Chem. & Ind.*, **1949**, 495

[203] *J. phys. colloid Chem.*, 1949, **53**, 1209
[204] Nellensteyn, F. J. and Baart, M. B. A., *J. Inst. Petrol.*, 1949, **35**, 302
[205] *Petrol. Processing*, 1949, **4**, 365
[206] *Petrol. Times*, 1949, **53**, 662
[207] Eliot, T. Q., Goddin, C. S., junr. and Pace, B. S., *Chem. Engng. Progr.*, 1949, **45**, 532
[208] *Oil Gas J.*, 1949, **48**, No. 5, 71
[209] Gard, C. D., ibid., **47**, No. 36, 56; *Gas*, **1949**, 30
[210] Littmann, E. R. and Klotz, J. R., *Ind. Eng. Chem.*, 1949, **41**, 1462
[211] *Oil Gas J.*, 1949, **48**, No. 9, 60
[212] *J. Inst. Petrol.*, 1949, **35**, 42
[213] Hulf, H. J., Rubach, A. and Withers, J. G., ibid., 485
[214] Crother, J. R., Pitkethly, F. E. and Stansfield, R., ibid., 245
[215] Downs, D., ibid., 784
[216] Rochnev, T. G., Carmichael, E. S., *Lubricating Engng.*, 1949, **5**, 15
[217] Coulter, G. L. and Borell, L. C., *Petrol. Refin.*, 1949, **28**, No. 3, 122
[218] Hughes, E. C., Bartleson, J. D. and Sunday, M. L., *Analyt. Chem.*, 1949, **21**, 737
[219] Pauls, J. T. and Goode, J. F., *Publ. Rds, Wash.*, 1948, **25**, 109

IRON AND STEEL

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EXPANSION and reconstruction, according to the 1946 Steel Development Plan, has progressed rapidly during 1949; a number of major schemes are now complete, and others are nearing completion and expected to come into operation during the coming year. The increased capacity already available, assisted by improvement in the supply of certain raw materials, notably imported iron ore, has contributed largely to the record steel output of 15,553,000 tons which was achieved in 1949.

It is apparent that the abnormally high demand for steel, which existed throughout the world during the immediate post-war years, has now passed its peak—a fact which is reflected in certain parts of the world by definite decreases in output. It is not expected that any similar reduction in output will follow in this country and, in fact, for certain types of steel—material for motor-car bodies for example—demand still exceeds supply. Nevertheless it is noticeable that demands from some other consumer industries, notably shipbuilding, are on the decline, and the ratio of orders to deliveries, according to recent data supplied by the British Iron and Steel Federation, has fallen markedly during the year. It follows, therefore, that whereas until the beginning of 1949 all effort was concentrated on increasing production, it is now more necessary to provide flexibility of output, with respect to the types of material produced, so that the fluctuating demands of the consumer industries may readily be met.

To compete successfully in the world markets it is imperative also that production costs should be kept as low as possible. At present, British steel prices are among the lowest in the world, but if this position is to be maintained, more attention must be paid to productivity, i.e. output per man as distinct from total production. Many lessons on this important subject have been learnt by the various teams which have visited America, under the auspices of the Anglo-American Council of Productivity.

To summarize, the immediate objective of the British steel industry must be to provide a flexible supply, which is able to respond quickly to changing demands both at home and abroad, while production costs are kept as low as possible by means of increased productivity, resulting from improved technical efficiency and more efficient use of available labour.

Mineral resources and treatment of iron ores

Although the tremendous mineral resources of the Minas Geraes region of Brazil have been known for a very long time, it is only recently that the Brazilians have realized the necessity of fully exploiting these potentialities. Of particular interest are the large deposits of very rich iron ore, whose strategical importance to the Western World is emphasized by Vaill.[1] The richest of these ores is a hæmatite containing

68 to 70% iron. It is estimated that the total iron ore deposits of this region would be sufficient to meet world requirements for the next 100 years. So far, however, various economic and political difficulties have hindered anything like full development, but it is hoped that these difficulties will be overcome and the ore made available for economic export. Meanwhile, the metallurgical industry in Brazil is considering the possibility of increased internal development of their own mineral resources. There are, for instance, various schemes[2] for developing cheap hydroelectric power for electric smelting both of pig iron and ferro-alloys, since, in addition to its iron ore deposits, Brazil also has large resources of other alloying elements, which it is now considered[3] may more profitably be exported as ferro-alloys rather than as the raw minerals.

In other areas, where the supply of rich ores is fast diminishing, attention continues to be devoted to improving methods of ore concentration and utilization of lean ores. In many parts of the world, there are very large resources of iron as taconite, which is essentially iron-bearing quartz containing only 25–30% iron. Taconites are found both in magnetic and non-magnetic forms and, since the concentration processes used in general depend upon magnetic separation, the non-magnetic varieties require an initial roasting procedure to convert the iron oxide components to magnetite. In all cases, because of the intimate association with quartz of the iron-bearing constituents, it is necessary to crush very finely to effect separation and the resulting concentrate must then be agglomerated either by sintering or briquetting, or as is now being considered[4] in Norway, by pelletizing. Howard[5] has recently suggested a simplified procedure for taconite utilization which eliminates any concentration process, either flotation or magnetic separation, before reduction, and reduces the degree of crushing required. Essentially the proposed method is to grind to moderate size (40 to 60 mesh), briquette with ground coke or coal and heat in a tunnel or rotary kiln at 1370° c. for a few hours. The resulting product is a friable mass of quartz containing globules of metallic iron which may then be magnetically separated.

At the 1948 meeting of the Blast Furnace, Coke Oven and Raw Materials Committee, there was a session[6] on sintering-plant design and operation in the United States. Although the various plants and practices described differed in detail, all more or less conformed to one or another of the standard sintering techniques.

The Committee on Sintering[7] of the Spanish Iron and Steel Institute proposes to carry out extensive research on the sintering of Spanish ores. Among other suggestions is one that the possibility of sintering, using upward blowing instead of down-draught suction, might be investigated; the fans would then be handling cold air instead of the corrosive hot gases from the sinter bed. It is also anticipated that higher pressure differences might be obtained with blowing than with suction.

An extremely modern and efficient plant has recently been installed at Corby[8] for the preparation of local Northamptonshire iron ores for the production of phosphoric pig iron to be used in the basic-Bessemer process. The plant is designed for the crushing, screening, bedding and reclaiming of approximately 1000 tons of ore per day. The lump ore and fines are separately bedded, and blending is designed to give approximately a

1 : 1 ratio of silica to lime in the burden, whilst ensuring a sulphur content not exceeding 0·3%.

Since Britain has ample supplies of vanadium, from relatively rich raw materials such as the vanadium ores of Northern Rhodesia and South-West Africa or from fuel oil soots rich in vanadium, little attention had been given to the vanadium contents of native iron ores, until Deans,[9] on behalf of the Mineral Resources Department of the Imperial Institute, carried out an extensive survey of the subject. It was found that the four main Jurassic ironstone deposits in this country, those of Northamptonshire, Lincolnshire, Leicestershire and Cleveland, which provide 95% of the domestic iron ore production, have average vanadium contents ranging between 0·035 and 0·07%; whereas in the Cumberland and Glamorgan hæmatite deposits, no vanadium was detected. In the blast furnace practically the whole of the vanadium content of the burden is concentrated in the metal; this means that in the basic irons produced from the Jurassic ores there is an appreciable vanadium content, and during the oxidizing conditions of the subsequent steel-making procedures, either open hearth or Bessemer, it is completely oxidized to the slag, to be either discarded on slag heaps or used as fertilizer.

Although it is not envisaged that recovery of vanadium from these sources would be economically acceptable, unless special circumstances demanded it, the possibility of doing so was demonstrated in Germany during the war,[10] when nearly 3000 tons of vanadium/yr. were recovered from iron and steel plant slags containing about 0·1% vanadium. The German methods of vanadium recovery were based on an alternate double process of reduction in the blast furnace and oxidation by air in either Bessemer converters or steel tube furnaces, to yield a slag containing 7–10% of vanadium. This slag was roasted with soda ash or sodium chloride and the resulting sodium vanadate extracted in water. Vanadium pentoxide or calcium vanadate was then precipitated, by addition of acid or lime respectively, and the product smelted to yield ferro-vanadium.

Production of pig iron

The major technological modifications of the blast furnace process, namely oxygen enrichment of the blast and high top-pressure operation, which were discussed in some detail in the 1947 and 1948 Reports, have not as yet found favour in this country. In fact, their possibilities do not seem to have been investigated on any extensive scale. In the case of oxygen enrichment, the reason is evident, since there is no prospect of its economic use in pig iron production until tonnage oxygen is available at a fraction of the present price of high-purity oxygen. The reasons for the failure to adopt high top-pressure operation, or at least to examine its potentialities, are not so apparent, but there are practical reasons why the use of high top-pressure may not be so beneficial in lean ore practice, which constitutes the major proportion of British output, as in rich ore practice.

An interesting development, that has been initiated in this country, is the use of carbon bricks in the blast furnace stack. Arising from an investigation of the incidence of scaffolds in blast furnaces operated on

lean ores, and the discovery that sticking of the burden to the furnace lining, which is at least in part responsible for scaffold formation, did not occur if carbon bricks were used, it was decided to carry out a large-scale trial of carbon bricks in the stack of one furnace at Appleby–Frodingham.[11] Although the benefits of carbon refractories, for the hearths of blast furnaces, have been recognized for some considerable time, the use of carbon for lining the stack was a completely new venture. The obvious danger in such a practice was that combustion of the lining might occur; however, the furnace under investigation with a 15-ft. section of carbon in its stack has now been in successful operation since 1946. It is suggested that the freedom from combustion hazard, upon which depends the success of carbon linings for the stack, may be attributed to the fact that, whatever the temperature or carbon dioxide content of the gases, they have always been in contact with coke at a higher temperature before reaching the lining.

The technique of compensated charging in the blast furnace, on which preliminary experiments by Saunders and Wild were mentioned in the 1948 Report, has now been extended to trials on an experimental furnace.[12] This experimental furnace, constructed and operated under the auspices of the Iron Making Division of the British Iron and Steel Research Association, and situated at Shelton Iron, Steel and Coal Co., Ltd., is described in detail by Saunders, Butler and Tweedy.[13] It has a hearth diameter of 21½ in. and output is at the rate of one cast of 5–8 cwt. every 4 hrs. The experiments on compensated charging in this furnace provide general confirmation of the laboratory findings and it is concluded that the new design of bell and hopper, which has been developed to permit any desired radial distribution of the charge, can be operated so that channelling, due to segregation, is minimized and gas/solid contact in the furnace correspondingly improved.

Optimum conditions for desulphurization in the blast furnace still provide a fruitful subject for conjecture and experiment. An interesting review of this subject, with particular reference to the effects of sulphur in the coke, and the associated subject of ash content of coke has been given by Lowry.[14] Here, the view is expressed that, whereas these two factors are frequently blamed for most of the irregularities in blast furnace operation, a more systematic investigation might show that this blame was not always justified. The direct disadvantage of high ash content in the coke is the increased fuel consumption required to melt the extra slag bulk, resulting from the ash and the additional limestone used to flux it. In addition to this increased thermal burden on the furnace, there is also the disadvantage of more uneven operation, resulting from increased basicity of the slag in the bosh zone, since the slag does not attain its desired final composition until the acid ash content of the slag is released in the combustion zone of the hearth. Suggestions that this condition might be alleviated by injection of limestone into the tuyère zone are quoted.

With respect to sulphur it is shown that the extra slag bulk, and therefore the increase in fuel consumption is, for a given increase in the sulphur content of the coke, about 25% greater than for the same increase in ash content of the coke. It is pointed out that although both high ash and

high sulphur contents in coke have their attendant difficulties, these are by no means as serious as the troubles which accrue from variations in these factors.

Although it is admitted that the composition of blast furnace slags has considerable bearing on their desulphurizing power, the most important variable is believed to be temperature. The fact that, in practice, a more basic slag gives better desulphurization does not contradict this conclusion, since in order to maintain adequate fluidity it is necessary to raise the temperature as the basicity of the slag increases.

The improvement in desulphurization with increase in temperature is well recognized, but it does not give rise to a generally acceptable method of desulphurization, as the increased silicon content of the iron, which accompanies an increase in temperature, is not desirable in subsequent open-hearth steel-making. An alternative method by which efficiency of desulphurization might be improved would be to increase the time of contact between slag and metal. Data are quoted showing that furnaces have operated for long periods with sulphur contents of 3–4% in the slag giving iron containing only 0·04–0·05% sulphur; this makes untenable the widely held view that the saturation value for sulphur, in blast furnace slags, is of the order of 2%. It is suggested that the efficiency of slag-metal reactions in the blast furnace may be largely governed by the dimensions of the central inactive core, which provides a surface over which the liquid iron and slag may run in intimate association, and therefore affords the opportunity for slag–metal reactions including desulphurization. If this theory is accepted it is apparent that the furnace should be operated so that the top of the inactive core is just below the level at which both iron and slag become completely molten. By careful attention to this and to other operating variables, it should therefore be possible to produce low-sulphur iron at temperatures low enough to avoid undesirable increase in silicon content.

The importance of the time factor in desulphurization by blast furnace slags is confirmed by the investigations of Hatch and Chipman,[15] who show that the sulphur contents of pig iron found in practice are always higher than the equilibrium values for the same conditions. They deduce therefore that improvements in desulphurization are controlled by the kinetics, rather than by the thermodynamics of the transfer of sulphur from metal to slag, and attention is drawn to the importance of the work of Chang and Goldman, mentioned in the 1948 Report, on the mechanism of sulphur transfer from slag to metal. It is suggested that a thorough study of various methods of mixing slag and metal might indicate some simple technique whereby the need for other desulphurizing agents would be eliminated.

Regarding the actual equilibrium distribution of sulphur between metal and slag, Hatch and Chipman show that on a molar basis, magnesia is only two-thirds as effective a desulphurizing agent as lime, which means that on a weight basis they are about equally effective. In general alumina and silica reduce the desulphurizing power of slags to a similar degree, although in more acid slags alumina is rather less detrimental than silica.

Oelsen and Maetz[16] report an interesting laboratory investigation of the possibilities of desulphurization in the blast furnace by the formation of

silicon sulphide. It was found that addition of quartz to a pig iron melt caused the evolution of silicon sulphide diluted with carbon monoxide; silicon sulphide evolution resulted also from addition of ferro-silicon but not until the silicon content of the melt was higher than was necessary with quartz. Under the most favourable conditions, however, the silicon content of the melt had to be raised to 10% before sulphur could be reduced to 0·05%. Obviously, therefore, in normal blast furnace practice, the formation of gaseous silicon sulphide plays no important role in desulphurization.

In spite of the vast amount of investigatory work that has been carried out and the very real advances that have been made in our understanding of the chemistry of the blast furnaces processes, it is still possible to find diametrically opposed opinions on the desirability of some particular procedure or set of conditions. Thus, for example, Korobova and Korobov[17] in Russia claimed that the presence of hydrogen in blast furnace gas had very definite advantages, because of its catalytic action on the reduction of iron ore at temperatures above 840° c., and that addition of 2—9% steam to the blast, to provide the desired hydrogen, substantially reduced the coke rate. Conversely, in France Boissin[18] has recently presented data to show the detrimental effect of hydrogen in blast furnace gas, claiming that an increase of 1% in the hydrogen content of blast furnace gas increased coke consumption by approximately 1 cwt./ton of iron. These divergent opinions are, however, perhaps not quite so irreconcilable when it is noticed that the Russian workers admit the necessity of increasing blast temperature when steam is introduced with the blast. This is to compensate for the heat required to dissociate the steam and amounts to 74° c. for each 1% steam added. The alleged saving in coke must therefore be counterbalanced, at least in part, by increased consumption of blast furnace gas for preheating the blast, leaving a correspondingly smaller amount available for other purposes. On the other hand, if the blast temperature were not increased, the hearth temperature could be maintained at the required level only by increasing the coke rate, as was apparently found by Boissin. Another advantage claimed for the introduction of steam to the blast was that it widened the oxidizing zone of the furnace and thereby gave more uniform working and eliminated hanging: this aspect may well be worth consideration.

The laboratory work of Herzog,[19] on the physical and chemical changes occurring during the heating and reduction of iron ores and sinters, is of interest as much for the novelty of the technique used as for the results obtained. Essentially the method employed was to use change in volume of the material under examination, as measured by a dilatometer, to indicate the changes in chemical composition during treatment. The dilatometric measurements, of course, only indicated the temperature at which changes occurred, the nature of the change being determined by chemical analysis. It was found that increase in volume was associated with (i) loss of chemically combined water at 400–450° c., (ii) dissociation of calcium carbonate between 650 and 700° c. (this was observed in two ores only), (iii) reduction of a compound of CaO and Fe_2O_3, and (iv) carbon deposition at 500–600° c. Contraction occurred when iron carbonate

dissociated at 550–650° C., when calcium carbonate dissociated at 800–930° C., and at higher temperatures as the result of iron oxide reduction and metal flow. Of factors affecting reducibility it was found that swelling, with consequent increase in porosity, and carbon deposition assisted reduction, whereas evolution of carbon dioxide had the expected effect of hindering reduction.

At the very important discussion on 'The Physical Chemistry of Process Metallurgy' held by the Faraday Society in September 1948, one session was devoted to the subject of roasting and reduction processes. Most of the papers presented were of general interest to both ferrous and non-ferrous metallurgists but special attention might perhaps be drawn to two contributions of particular interest in relation to the theory of blast furnace operation. The first of these, a paper by Woods[20] on the possibility of regarding the reduction of iron ores as a diffusion-controlled reaction, concludes that this is a reasonable assumption, except possibly in the case of very dense hæmatite, but that pore systems found in practice are so very complex that it is difficult to predict the reducibility of a particular ore from normal porosity measurements. The second was an account of the experimental work, carried out by Juliard, Rayet and Ludé,[21] on the catalytic effect of various solid phases on the deposition of carbon during the reduction of metallic oxides with carbon monoxide. The two oxides studied were NiO and Fe_2O_3 and the course of their reduction with carbon monoxide was followed by continuously recording the weight of the sample and the flow of gases (i) into the reaction chamber, (ii) at the exit from the reaction chamber, and (iii) after absorbing carbon dioxide from the exit gases. In this way it was possible to measure simultaneously the rate of reduction of the oxide according to the reaction $MO + CO \rightarrow M + CO_2$, and the rate of carbon deposition according to the reaction $2\ CO \rightarrow C + CO_2$, enabling a more precise determination of the kinetics of the latter reaction than has previously been possible. From the results obtained, it was concluded that the deposition of carbon is catalysed neither by pure nickel nor by pure iron, but by metallic nickel or iron in the presence of another solid phase, for example, carbon or NiO in the case of nickel, and FeO, Fe_3O_4 or Fe_3C in the case of iron. It was found also that the carbon deposition reaction was catalysed by nickel charged with hydrogen.

An interesting new technique for determining the gas velocity, at various positions in the cross-section of a blast furnace, is described by Voice.[22] The method depends upon the use, as tracer, of a small quantity of radioactive gas injected through the tuyères. Samples of gas at various positions in the furnace are then taken at regular time intervals, and measurements of the radioactivity of these samples is used to calculate the transit time for the gas through the furnace. It is essential that the radioactive material used for this purpose should be an inert gas, so that it passes unchanged through the furnace; for the experiment, radon was used. To date, preliminary experimentation only has been carried out, but this has been reasonably successful and the author expresses the hope that other investigators will be encouraged to experiment on similar lines.

Foundry practice

Current research by the British Iron and Steel Research Association (Steel Castings Division) and the British Steel Founders' Association, on the manufacture of steel castings, has been briefly surveyed by Bishop and Lewis.[23] Although it is obviously not possible to review here the whole research programme of these two associations, some of their more important contributions to foundry knowledge will be discussed in the course of the report.

An important problem in most steel foundries is the high sulphur content of pig iron from the cupola, and consequent need for external desulphurization. Soda ash treatment in the ladle, which is the method generally employed, is not entirely satisfactory and soda ash is in short supply. Alternative methods of desulphurization have therefore been investigated by the Steel Castings Division of B.I.S.R.A.[24] It is concluded from these investigations that the essential features of a satisfactory desulphurization technique are that the iron should be thoroughly mixed with a highly basic and fluid slag under reducing conditions. Of the methods examined, the addition of a mixture of limestone and calcium nitride, in approximately equal proportions, gave the most promising results. The vigorous evolution of gas, resulting from this addition, promoted efficient mixing of slag and metal but some difficulty was experienced in maintaining adequate fluidity in the slag. Investigation of this and other methods is continuing.

With the increasing practice of desulphurization of cupola pig iron in the ladle, and particularly the current use of sodium carbonate for this purpose, it has become apparent that the use of acid-lined ladles is frequently uneconomic because of the excessive wear and decreased life resulting from alkali attack. A committee of the Institute of British Foundrymen[25] is therefore investigating the use of basic lined ladles where desulphurization with sodium carbonate is practised. Work so far has shown that not only is ladle life improved but also desulphurization is more efficient when basic linings are used. It is recommended that fired stabilized dolomite bricks should be used, and modifications and precautions required in operational technique to ensure maximum benefits are indicated. Although this particular research was concerned primarily with sodium carbonate desulphurization, the use of basic lined ladles would obviously be advantageous for any method of desulphurization depending upon the use of a basic slag.

In side-blown converter practice it is found that in addition to the expected refractory wear of the tuyères and of the front wall opposite the tuyères, there is also serious erosion of the back wall immediately above the tuyères. In order to investigate the cause of this, and possible means of prevention, a small-scale transparent model converter was built by the Physics Department of B.I.S.R.A.,[26] so that the movements of metal, slag and blast, under various operating conditions, might be studied. The model was operated at room temperature with the steel bath simulated by water or other suitable liquid. It was found that erosion of the back wall above the tuyères could be attributed to recirculation of gases in the converter, resulting inevitably from entrainment of the surrounding atmosphere by the incoming turbulent blast jets.

Modifications in converter design are suggested, either for preventing this recirculating gas from coming into contact with the walls of the vessel, or alternatively, for minimizing erosion by the recirculating gases by modifying the shape of the walls. In the former category was the suggestion that tuyères should be situated on opposite sides of the vessel so as to impart a helical spin to the outgoing gases; it was found that in this way the back eddy could be confined to the centre of the chamber. In the latter category was the introduction of an outward bulge in the back wall above the tuyères, which enabled the recirculating stream to approach the blast jets without undergoing so violent a change of direction when it actually entered the jets, so that erosion of the wall was reduced. It is intended to continue this investigation first on a small-scale converter operating with hot metal and then on full-scale converter operation.

It is of fundamental importance in all types of casting to use risers of correct design in the correct position. Because of the infinite variety of shapes and sizes of castings, the tendency has been to regard this as a problem which could be approached on empirical lines only. Caine[27] now claims, however, that if the subject is divided into the two aspects of positioning and dimensioning then it is relatively easy, no matter how complex the casting, to obtain quantitative data on both aspects, which will make possible accurate riser design. For the purpose of riser positioning, each casting should be considered as being divided into a number of sections, each of which can be adequately fed by one riser; each riser and that part of the casting within the feeding range of the riser may then be regarded as a separate simple system, independent of the rest of the casting. It is pointed out that risers have two functions, namely to supply the required liquid feed metal to the solidifying casting and to provide the hydrostatic head of metal needed to avoid certain types of shrinkage cavity. This latter requirement depends entirely upon the height of the riser. The fundamental equation suggested to give correct riser dimensions is :—

$$x = \frac{a}{y - b} + c$$

where x is the freezing ratio (i.e. ratio of surface area to volume for the casting ÷ ratio of surface area to volume for the riser) and y is the volume of the riser; a, b and c are constants. The simplest form of the equation for steel has been established as :—

$$x = \frac{0{\cdot}12}{y - 0{\cdot}05} + 1{\cdot}0$$

By plotting the values of x and y that satisfy this equation, a curve is obtained from which the required riser dimensions may be derived.

If insulated risers or exothermic pipe eliminators are used, the value of constant c, in the above equation, is decreased, giving a corresponding decrease in the size of the riser required for a given purpose. Colditz[28] discusses a process of pipe elimination in steel founding, depending upon the exothermic reaction between aluminium and iron oxide. In addition to these main constituents the 'thermit' pipe eliminator contains other

ingredients, such that the product from aluminium reduction is of similar composition to the steel being cast; this is necessary as some of this metallic product may become incorporated in the actual casting. The heat of reaction of the eliminator, which is added to cover the open end of the riser, keeps the metal fluid for longer than would otherwise be possible, with the result that a smaller riser can be used and metallic yield correspondingly increased.

The most important advance of recent years in cast iron metallurgy is undoubtedly the development by the British Cast Iron Research Association of cast iron which is ductile in the 'as-cast' condition. This discovery, which was published last year by Morrogh and Williams[29] has been followed by extensive research and development work both in the laboratory and on the foundry scale. The required ductility is achieved by adding certain elements, which cause the iron to freeze with its graphite precipitated as nodules instead of in the usual lamellar form. In this type of structure, the discontinuities in the metallic matrix are less extensive and stress distribution is more uniform, with the result that the product is ductile and of much higher tensile strength than normal cast iron. The magnitude of the improvement which has already been attained is indicated by Donoho,[30] who records the production of ductile cast iron, which without any heat treatment had a tensile strength of 75,600 lb./sq. in. with nearly 20% elongation; this may be compared with normal cast iron having a tensile strength of about 20,000 lb./sq. in. and little or no ductility. In the original work of Morrogh and Williams, the desired nodular graphite structure was produced by treatment with cerium. The precise mechanism of the process was not completely understood, though it was suggested that desulphurization by the cerium addition played an important part.

It has been suggested[31] that lamellar precipitation of graphite is promoted by the presence in the liquid iron of hexagonal nuclei in suspension, as is the case when solid silica occurs as a product of deoxidation of the iron. On the basis of this assumption, lamellar graphite precipitation could be prevented by adding an element of stronger deoxidizing power than silicon which does not give products, i.e. oxides, carbides and nitrides, of hexagonal crystal structure. Cerium is one such element, and others suggested are magnesium, lithium, calcium, strontium and vanadium. Whereas this theory could account for many of the facts, it does not explain the marked hindering influence of sulphur on nodular graphite formation.

Of the elements other than cerium, the greatest attention has been paid to the use of magnesium as a promoter of nodular graphite precipitation. Donoho[32] has studied this application of magnesium in considerable detail and has shown that the presence of 0·03–0·10% magnesium in the iron gives a nodular graphite structure. Experiments were carried out both with additions of pure magnesium and of various alloys of magnesium; it was found that the best results were obtained when copper or nickel alloys of low magnesium content were used. Unlike cerium, the efficacy of magnesium is apparently unimpaired by high contents of sulphur and phosphorus or a low carbon content in the iron. For any particular composition of cast iron, there is an optimum content

of magnesium, below which a mixed structure is formed and above which the material becomes excessively hard and brittle.

Although rapid progress has been made in this new field of ductile iron production, there are many problems still to be solved. As pointed out by Reese,[33] in a general survey of the subject, it is not possible without considerable modification to apply existing cast iron founding technique to the production of ductile iron castings ; to quote one example only, it is necessary to change the dimensions of gates and risers because of the altered freezing characteristics of the new material. There are of course many other factors, both technical and economic, which will require careful consideration.

Production of steel

Plant.—'The criterion by which a lay-out can be judged is the extent to which it permits efficient handling of materials between the unit processes, and the efficient working of the processes themselves.' Starting from this premise, Mardon and Terrington[34] have carried out a survey of many of the most important integrated iron and steel plants in Great Britain, with a view to providing fundamental rules, upon which plant lay-out may be based to give maximum efficiency. Because of the complexity of the subject and the special factors requiring consideration in individual works, it has not always been possible to formulate rules which would be applicable under all circumstances ; nevertheless a number of very useful conclusions have been drawn. The scientific approach to this problem, which too often in the past has been allowed to solve itself, is a definite forward step, and it provides useful guidance for the construction of new works and for the improvement of existing plant.

The section of the 1946 Steel Development Plan concerned with increasing steel-making capacity is well advanced. The new melting shop at Appleby–Frodingham,[35] comprising two 300-ton tilting furnaces and one 600-ton active mixer, has been in operation for two years. During its first full year's operation, the total output from this shop was 216,636 tons. Nearing completion and expected to come into operation before the end of 1949 is the new melting shop at Round Oaks.[36] This is to consist of five 100-ton Venturi type furnaces which will increase the ingot capacity from 160,000 to 250,000–300,000 tons/yr. Construction is proceeding also on the installation, at the Clydebridge Works of Colvilles,[37] of two additional 300-ton tilting furnaces, to give an estimated increase in output of 175,000 tons/yr. In addition to these major projects for increasing steel-making capacity, there has also been extensive reconstruction of the open hearth plant at the Clydesdale Works of Stewarts and Lloyds,[38] for the purpose of co-ordinating steel making and tube making. For tube making, steel of very high quality is required and careful control of melting and casting conditions is essential. It was decided that 60-ton furnaces could best provide the required conditions, and accordingly four furnaces of this capacity are now used.

One of the conclusions drawn by Chesters and Thring, from their work on 'The Influence of Port Design on Open Hearth Furnace Flames,'[39] was that there was an urgent need for further information regarding the gas flow patterns in open hearth furnaces. Following this recommendation,

Chesters and his collaborators have now, with the aid of models, filled many of the gaps in the existing knowledge of fluid flow in open hearth furnace systems.

As a preliminary to the more complex problem of flow in three dimensional open hearth furnace models, the flow in simple two-dimensional geometrical shapes was first investigated.[40] For this purpose, shallow Perspex dishes of appropriate shape were used with water introduced through jets and allowed to escape over weirs. Several different methods of visualizing the flow in these simple systems were investigated, but it was found that the best results were obtained by using bakelite powder floating on the liquid surface. As admitted by the authors, most of the conclusions drawn from this part of the investigation were already familiar to specialists in fluid flow, but they served the very useful purpose of clarifying the field prior to the investigation of more complex problems.

In order to make possible the study of flow in three-dimensional furnace models, it was necessary to develop special techniques of visualization and photography.[41] Several different techniques were employed, each having its own peculiar merits depending upon the conditions and the information required.

The final section of the work, on flow of water through Perspex models of open hearth furnaces,[42] showed that comparatively small changes in certain features of design could cause marked modifications in flow pattern. In view of the inability of water models to take account of combustion effects, which must be of material importance in full-scale operation, it is a matter for some conjecture as to how far flow patterns in water models may be taken as indicative of the gas flows occurring in actual open hearth practice. It is encouraging to find, however, that preliminary experiments on the gas flow in production furnaces show many similarities to the flow patterns obtained in water models of furnaces with similar design characteristics. The authors express the hope and belief that in a few years' time the construction of a model on the lines of those investigated will be considered as a necessary preliminary to the construction of a new design of furnace.

A similar technique involving Perspex models has been used by B.I.S.R.A. to study fluid flow in the side-blown converter (*see* p. 101).

Collins and Tyler[43] describe a somewhat different approach to the use of models for studying flow in open hearth furnaces, with particular reference to the efficiency of gas and air mixing obtained by different port designs. The method employed was to inject air through both the air and gas ports of the model, with a small amount of CO_2 injected into the gas port to act as tracer. Samples of gas were then taken from specific positions in the model and analysed for CO_2, the CO_2 content being a measure of the proportion of air from the gas port present in the sample. In this way it was possible to assess the effect of modifications in design on the efficiency of mixing.

Thring has given a great deal of constructive thought to the heat-transfer aspect of furnace design. He concludes,[44] from the fact that the roof of an open hearth furnace tends to be hottest at the outgoing end, that the flames in general operation are too long. He acclaims the work that is being done on furnace models and expresses the opinion that the

objective should be to modify port design so that shorter flames are obtained. The length of furnace flames required to give maximum efficiency of heat transfer and fuel utilization is the subject of considerable controversy, but the opinions expressed by Thring are certainly worthy of very careful consideration.

Thring (*loc. cit.*) emphasizes also the improvements in output and efficiency which may be derived from increased instrumentation. In particular he mentions the benefits to be obtained from roof pyrometry (to ensure consistent working at the maximum safe roof temperature), and furnace pressure measurement (to ensure an adequate positive pressure, which will prevent excess cold air in-leakage with consequent deterioration in combustion efficiency). A new electrical pressure meter, developed in the Physics Laboratories of B.I.S.R.A., for the measurement of open hearth furnace pressures is described by Carlisle and Smith.[45] The new instrument is claimed to have marked advantages over existing types of pressure meter, particularly in respect of its simplicity of mechanical construction, stability of calibration and speed of response to pressure fluctuations. This latter quality makes it particularly suitable for incorporation in automatic control systems.

Practice.—An interesting statistical survey of the factors affecting output, in one specific basic open hearth furnace, has been published by Robertson and Thring.[46] The analysis is most comprehensive and contains much information which is of interest to basic open hearth steel-makers in general. It is shown that melting time is most closely correlated with the rate at which oil can be burned during charging and melting; the factor which has the greatest influence on total heat time, however, is the rate of oxidation of the metal during charging and melting.

Existing methods of charging open hearth furnaces are reviewed and their merits assessed by Diamond and Frankau.[47] It is concluded that the aim of any supply system and type of charging machine used should be to maintain an even rate of charging throughout the charging period; this should be the maximum uniform rate at which the furnace can accept the cold material, rather than an intermittent charge at a higher rate. The two types of supply system at present in use are stage railway systems and bench systems. Both systems have certain advantages, but on economic grounds bench systems are generally preferable, and it is suggested that future work on this subject should be devoted to the development of the bench type of system, with particular reference to improved methods of scrap handling, probably incorporating some form of conveyor system. It is possible also that new types of charging mechanism might be found to be desirable.

An original suggestion for facilitating open hearth furnace charging has been made by Gumpp.[48] It involves modifications in furnace design to allow the roof to be raised, either by hydraulic jacks or by an overhead crane. Charging platforms would be situated on either side of the furnace, extending for the entire length of the movable roof section. During the progress of a heat, scrap for the next heat would be loaded on to these charging platforms from which it could then be fed directly into the furnace when required, by tipping the platform.

Adequate control of sulphur is always a major problem in basic open

hearth steel-making and particular attention has recently been directed to the effects on this variable of sulphur in the fuel. Short and Meyrick,[49] at Normanby Park Steelworks, investigated the effect of sulphur content of fuel gas upon sulphur removal from the steel. Low-sulphur fuel was found to show slight benefits; the differences obtained however between high- and low-sulphur fuels were in no case really significant and the results varied widely, even with gases of similar sulphur content; consequently it was concluded that other factors exerted a greater effect on the efficiency of sulphur removal than did the sulphur content of the fuel.

On the other hand, during discussions at the 1948 Open Hearth Conference of the American Institute of Mining and Metallurgical Engineers, there appeared to be unanimity in the belief that the sulphur content of the fuel had an extremely important effect on the efficiency of steel desulphurization. Berner,[50] for instance, quoting data for 145-ton furnaces, claimed that using a high-sulphur fuel oil it was necessary to charge much more limestone, and removal of sulphur to the required level took about ½ hr. longer than with a low-sulphur fuel. Warren[51] had shown that most of the sulphur pick-up occurred during the melting down period, and for that reason considerable improvement could be obtained in shops with a supply of both coke-oven and natural gas, by melting down with the low-sulphur natural gas and refining with coke oven gas. Such a procedure is of course not practicable in this country where there is no supply of natural gas, but the importance of low-sulphur fuel, especially during the melting period, appears to have been definitely established.

An interesting new approach to the problem of dephosphorization has been provided by Maddocks and Turkdogan[52] who on the laboratory scale have used additions of sodium oxide to dephosphorize pig iron at 1400° C. In their introduction, the authors point out that, other things being equal, the removal of phosphorus is most efficient at low temperatures, i.e. of the order of 1400° C. When lime is used as the base for dephosphorization, however, it is not possible to obtain slags which are sufficiently basic and at the same time fluid at temperatures of this order. It was apparent therefore that an alternative base, giving a stable phosphate and fluid slags at lower temperatures must be sought; the use of sodium oxide, which seemed to be the most suitable, was investigated. In the initial experiments soda was added to basic slags, but this was found to be quite impracticable because lime in the slag replaced soda from the silicates and the freed soda was volatilized. In order to maintain the soda in the slag as silicates, it was obvious that an excess of silica was required and accordingly further work was devoted to the addition of soda to siliceous slags. It was found possible to remove 85% of the phosphorus present in a 1·34% phosphorus pig iron at 1400° C. by the use of a slag containing 30–35% SiO_2 to which soda had been added.

From the laboratory results it is suggested that soda–acid slags might be used with advantage in hot metal mixers, where the temperature is of the same order as the temperature investigated. Although not yet fully investigated, the indications are that dephosphorization might be carried out at steel-making temperatures by the use of a slag containing more than 50% SiO_2. Experiments on these lines in production-scale acid furnaces are proceeding.

The production of electric steel in this country has been reviewed by the Electric Process Sub-Committee of B.I.S.R.A.[53] In considering probable future developments, it is pointed out that an important part in any such developments must be played by the trends in the cost of electric power as compared with other fuels. The over-riding advantage of the electric process, however, is for the production of low-sulphur steels, particularly in view of the general trend towards increased sulphur contents of open hearth fuels. For this reason, attention has been given to the production of less specialized steels in the electric furnace. Using a single slag process, several firms have been able to produce such steels in the electric furnace at prices competitive with open hearth steel.

The use of oxygen in the electric arc process, already developed to a high degree in the U.S.A., is finding increased application in British electric steel-making. The two main uses of oxygen in electric practice are to accelerate scrap melting, particularly that which remains on the banks after the bulk of the charge is molten, and to effect carbon removal. There are two distinct aspects to the use of oxygen for carbon removal. One, which applies to the production of carbon and low-alloy steels, is to accelerate the removal of carbon and to make possible the production of lower-carbon qualities than can be made by normal refining methods. The other applies exclusively to the production of high chromium qualities, particularly stainless steels. In normal electric-furnace operation refining with ore, chromium oxidizes much more readily than carbon, so that little of any chromium charged remains in the bath at the end of the oxidizing period. If, however, the refining temperature is increased to 1700–1750° C., as is possible when oxygen is injected, because of the exothermic nature of the oxidation reactions, carbon is removed in preference to chromium, because of the change in the relative free energies of formation of the relevant oxides at the higher temperatures. By using oxygen injection for refining in this way, it is possible to obtain up to 90% yield of chromium from a charge consisting of 100% stainless steel scrap. Useful information on this aspect of oxygen usage in electric arc practice, from experience at one steel-plant in the U.S.A., is given by Eisaman.[54] Several electric furnace plants in this country are also now using oxygen for this purpose on the production scale, but as yet no detailed results have been published.

A comprehensive survey of Bessemer practice, both British and foreign, published as a special report by the Iron and Steel Institute,[55] provides an invaluable reference book on the subject. Graham,[56] in an article on the Bessemer process, devoted primarily to practice in the U.S.A., concludes that extensive research at present in progress may enable the Bessemer process again to achieve a position of great importance.

Constant effort is made to produce Bessemer steel of nitrogen content comparable with open hearth steel. A process which is claimed to have achieved this objective, using what is called a 'turbo-hearth,' has been developed by two American firms and is described by Bain and Graham.[57] In this process, American basic iron is blown in a partly closed side-blown vessel lined with magnesia. Chemical action is rapid, as in the normal Bessemer process, but the conditions are such that phosphorus may be removed without increase in nitrogen content. Typical performance

shows a reduction in phosphorus content from 0·292% in the charge to 0·017%, whereas the nitrogen content remains unchanged at 0·003%. There are still various operating difficulties to be overcome but confidence is expressed in the fundamental soundness of the process.

Factors affecting the quality of rimming steel ingots have been considered by Warchol,[58] who makes general recommendations for control of the steel-making process to give a structure with blowholes sufficiently remote from the ingot surface to avoid internal oxidation during reheating, i.e. to give a product which is suitable for rolling to rod, wire, strip or sheet.

An interesting experimental series of small rimming steel ingots has been prepared and studied by Binnie.[59] The object of the investigation was to determine the effect of mould wall surface on rimming action and ingot structure; hæmatite moulds, copper moulds and moulds partly and fully lined with refractory material were used. There was no appreciable difference between the ingots cast in hæmatite moulds and those cast in copper moulds, but it was found that the use of refractory-lined moulds reduced the depth of the rim to about one-half that obtained with a chill mould and gave a purer rim and more uniform core analysis. It is recommended that for general rimming steel production, refractory-lined moulds should be used in preference to chill moulds.

Theoretical metallurgy.—Of recent years, increasing interest has been taken in the thermodynamic aspects of slag-metal equilibria and reactions in solution, during the steel-making processes. Many useful contributions to our knowledge of these subjects, among others, and reviews of progress to date, were provided at the Faraday Society's Discussion on the Physical Chemistry of Process Metallurgy in 1948.

The concept of activity, though not itself new, has only recently found general use in the literature on the physical chemistry of steel-making; the review of the significance of activity in liquid metallic solutions, given by Chipman[60] at the Faraday Society's Discussion, was therefore most welcome. To illustrate the importance of activity considerations, the deoxidation of liquid steel may be quoted as an example. Early theories of deoxidation were concerned only with the decrease in the dissolved oxygen content of the bath produced by deoxidizing additions. It now becomes necessary, as pointed out by Chipman,[61] to consider also the effects of the deoxidizer upon the behaviour of the residual dissolved oxygen. In general, the presence of a deoxidizing element decreases the 'activity' of the residual oxygen and causes it to behave towards carbon, or other elements present, as though the dissolved oxygen content of the bath were lower than it really is. This effect is tentatively explained by Chipman on the basis of atomic orientation. Although some of the detailed conclusions are still the subject of controversy, the importance of the effect is generally recognized.

It is axiomatic that desulphurization during steel-making should be effected when the state of oxidation of the bath is low, that is at an early stage in the process when carbon is high. Whether carbon itself in any way increases the efficiency of desulphurization was not known, however, before the investigations of Kitchener, Bockris and Liberman.[62] These

investigations confirmed that desulphurization is most effective at high carbon contents, primarily because of the accompanying low oxygen activity in the metal, but also, to a certain extent, because carbon increases the activity of sulphur in the bath and therefore promotes the desulphurizing reactions.

Efficiency of sulphur removal is of course governed by the equilibrium distribution of sulphur between metal and slag, which, according to Carter[63] is most satisfactorily given by the expression :—

$$(S)/[S] = k(\Sigma(n_{MO}) \div [O])$$

where (S) is the sulphur content of the slag, [S] is the sulphur content of the metal, [O] is the oxygen content of the metal, k is a constant and n_{MO} is the number of g.-ions of all the metal oxides in solution. It follows from this that, in the free state, CaO, MgO, MnO and FeO can all desulphurize molten iron, but combination of these oxides, with acidic oxides present in the slag, causes a corresponding reduction in their desulphurizing power. Desulphurization may be assisted also by the presence of other elements such as manganese, carbon and phosphorus which decrease the solubility of sulphur in iron and therefore increase its activity.

There has been, and for that matter still is, considerable controversy concerning the constitution of liquid slags; according to one view, the classical view, slags consist essentially of compounds, but according to another, as postulated by Herasymenko[64] in 1938, the slag constituents are completely dissociated into ions; between these two extremes there are varying shades of opinion. There has still been no conclusive proof of the ionic theory and some speakers at the Faraday Society's discussion, notably Guggenheim[65] and Carter,[66] expressed the opinion that it was an unnecessary and irrelevant complication. Nevertheless, the electrical conductivity of slags, as determined for instance by Bockris, Kitchener, Ignatowicz and Tomlinson,[67] is definitely indicative of some kind of ionic constitution. This subject, among others, was considered by Richardson[68] in a useful general survey of the constitution and thermodynamics of liquid slags; Chipman and Chang[69] have written an interesting paper showing how various data on slag–metal and slag–gas equilibria may be interpreted on the basis of an ionic theory of slag constitution.

Properties

The great current interest in the mechanism of metallic deformation was reflected in Sir Andrew McCance's choice of 'The Plastic Behaviour of Solids' as his subject for the fourth Hatfield Memorial Lecture.[70] A topic of particular controversy, which comes under this general heading, is the mechanism of creep, considered in some detail by McCance, who refutes all theories in which creep is regarded as a consequence of plastic flow. In his opinion creep occurs entirely as the result of atomic diffusion processes and in his lecture it was shown mathematically how the phenomenon of creep under constant load might occur as the result of two diffusion processes occurring simultaneously, viz. axial diffusion in which atoms migrate along the axis of the bar under load and cross-sectional or contractional diffusion in which atoms migrate from the

outside towards the centre of the bar under a stress-gradient. The most important conclusion to be drawn from this theory of creep is that it makes untenable the concept of limiting creep stress, since in theory any load however small must ultimately cause fracture, although the time to fracture may be so long, that for all practical purposes the stress may be considered safe.

One recent theory, which is at variance with the above views of McCance, is that of Wilms and Wood,[71] who have compared the mechanism of deformation under load at elevated temperatures with that at normal temperatures. These authors conclude that, at normal temperatures, deformation occurs as the result of slip and breakdown of the grains to crystallites of sub-microscopic size, whereas, at higher temperatures, deformation, i.e. creep, results from dissociation of the grains into relatively coarse particles allowing flow to occur by movement of these particles within the parent grains. In support of this theory it is claimed that these particles, or 'cells' as they are termed, may be observed and measured.

The various theories which seem theoretically capable of explaining creep phenomena have been critically examined and their merits assessed by Mott.[72]

It is now well known that the addition of small amounts of boron to certain types of steel improves their hardenability though the reason for this is not fully understood. After careful investigation, Digges, Irish and Carwile[73] conclude that the increased hardenability results from retardation in the rate of nucleation of ferrite and carbide caused by the presence of boron in solid solution in the austenite. Consequently, it is only boron in solid solution, as opposed to that which is undissolved or present as compounds, that has any effect on hardenability. Since, at heat-treating temperatures, it is possible to hold only a very small amount of boron in solution, maximum benefits with respect to hardenability may be obtained by very small additions of boron.

Comstock[74] has investigated the joint use of boron and titanium in various types of low-carbon steel ranging from plain carbon to 18% Cr, 11% Ni material. The plain carbon steels gave greater hardness with additions of both titanium and boron than with either element alone, whereas the tensile properties of the alloy steels were greatly improved by the presence of 0·2–0·4% titanium together with 0·02–0·03% boron.

Investigating the effect of boron on the mechanical properties of a range of low-carbon, low-alloy steels, Bardgett and Reeve[75] obtained the most outstanding results from boron addition to steels containing 0·30–0·40% molybdenum. One steel of this type, containing 0·14% carbon, 0·40% molybdenum and 0·003% boron was found to have particularly desirable properties, giving a maximum stress of more than 40 tons/sq. in. and a yield stress of 30–33 tons/sq. in., with good ductility and toughness; a similar steel, containing no boron, gave a maximum stress of only 30·4 ton/sq. in. and yield stress of only 16·9 tons/sq. in. The tremendous increase in yield strength resulting from boron addition renders this material particularly suitable for structural purposes, since the size of section used in construction may be substantially reduced with corresponding savings in weight and material. The possibility of producing

this type of steel on the commercial scale has been confirmed, several casts having been made successfully both in high-frequency and basic open hearth furnaces with boron additions to the ladle.

Boron has also been found to have important effects on the properties of cast iron. Krynitsky and Stern,[76] studying the effects of adding up to 0·48% boron to grey cast iron, showed that it exerted an under-cooling effect during solidification, increased the susceptibility to chill and in general gave increased hardness. The presence of boron also caused modifications in structure, notably by decreasing the amount and size of the graphite flakes and increasing the amount of free carbide. From an investigation of the effects of boron additions on the malleablization of white cast iron, Micksch, Fabert and Cover[77] conclude that, for maximum acceleration of annealing, the optimum content of boron is probably between 0·0012 and 0·0025%.

The influence of size, shape and distribution of non-metallic inclusions on mechanical properties is a subject requiring considerable elucidation, though, as the result of much systematic investigatory work, many fairly clear correlations between mechanical properties and non-metallic inclusions can now be drawn. Stewart and Williams,[78] to provide data for the guidance of U.S. naval inspectors, studied the effects of non-metallic inclusions on the endurance properties of steel and as a result are now able to specify the types and distribution of inclusions most likely to cause trouble in machine parts. The effects of inclusions on certain other properties have been studied by Eugène,[79] who showed that the most severe adverse effect of inclusions is seen in the transverse properties of rolled steel; for example, fracture in a transverse tensile test invariably started at an inclusion. Inclusions in general, and particularly those which have been elongated by rolling, increase susceptibility to quenching cracks.

It has been shown by Sims, Moore and Williams[80] that the presence of high hydrogen content in steel causes a marked decrease in ductility. The effect is not permanent, however, since by ageing at a moderate temperature, so as to eliminate all but a trace of hydrogen, the ductility can be completely restored. This temporary decrease in ductility may probably be explained by the decreased cohesion of the metal, which as shown by Bastien and Azou[81] results from the presence of hydrogen.

Metallography

Only of recent years has the value of the electron microscope as a metallographic instrument become generally recognized, but already great advances have been made in the technique of its use for this purpose. Merriman's general survey[82] of the construction and operation of the instrument, in which he compares its advantages and disadvantages with those of the optical microscope, is therefore of particular interest. The limitations of the electron microscope, with respect to resolving power and contrast in the image, have been calculated by Scherzer.[83] So great is the interest in the metallurgical application of the electron microscope that the Institute of Metals, together with other interested bodies, organized a symposium on the subject. This was held in November, 1949, so that a detailed report is not yet available.

While admitting the advantages of the electron microscope, particularly of its increased resolving power, Cuckow[84] has shown that certain of the other advantages associated with higher resolving power in the electron microscope may also be achieved with the optical microscope if a suitably modified technique is employed. For instance, a study of the variations in depth on the etched surface of a specimen provides a direct measure of the differential etching of the various phases present, from which may be derived much useful metallographic information. The electron microscope is able to provide such information because variations in thickness of the replica film, resulting from surface irregularities, are reflected as variations in brightness of the electron micrograph. As normally operated however the optical microscope gives no information concerning surface contours, but it may be enabled to do so by a modified technique, known as phase-contrast microscopy, in which the surface variations appear as interference fringes produced by light reflected from the surface of the specimen and from a plane surface almost in contact with the specimen. Relatively minor modifications are required to enable the ordinary optical microscope to operate on the phase-contrast principle.

Colour metallography provides much information that is not easily obtained from the usual black and white micrographs and Forgeng[85] gives details of a technique for the preparation of suitable colour micrographs.

A necessary preliminary to any metallographic examination is to polish the specimen satisfactorily and an interesting study of the physical properties required in metallographic polishing powders has been carried out by Rollason, Sharratt and Roberts.[86] It is concluded that the shape of the powder particles is the most important factor contributing to successful polishing and that a powder composed of plate-shaped particles is most suitable; granular materials should be avoided since they scratch the surface of the specimen. Of a series of oxides investigated, alumina, obtained by calcination of alum, was found to be most satisfactory, either in the α- or γ-form depending on the temperature of calcination; ordinary commercial α-alumina is granular, however, and therefore unsuitable for polishing. The p_H of the polishing suspension must be carefully controlled between 7 and 9 to avoid etching.

The austenite–martensite transformation has for a long time been a subject of study, and during the past year some valuable new quantitative data have been published. In Russia, Kurdyumov and Maksimova[87] have studied the kinetics of the transformation, which for the purpose of this investigation they caused to occur at a measurable rate by cooling rapidly to a very low temperature below the martensite point (it was found that by cooling to $-194°$ C. the austenite structure was fully retained), and then slowly warming again until transformation to martensite started. The rate of the transformation was determined by magnetometric measurement of the martensite.

Some doubt has been expressed as to whether austenite really decomposes isothermally at temperatures below the Ms temperature, as distinct from the transformation which occurs during the quenching operation. Thompson and Jepson[88] provide conclusive evidence of such isothermal

transformation and show that it may be detected even when the temperature is slowly rising. In the opinion of these authors, it is important to consider independently the transformation which occurs subsequently, though it is believed that the mechanism of martensite formation during isothermal decomposition is essentially similar to that causing martensitization during quenching, i.e. that the transformation results from the movement under stress of some definite crystallographic plane. There is no evidence, however, to show that it is the same plane that is affected during quenching and during isothermal transformation.

In this connexion the same authors[89] have studied the effect of imposed stresses on the rate of isothermal transformation. Tensile stresses of the order of 10 tons/sq. in. were found to give a marked increase in the transformation rate, but compressive stresses needed to be considerably higher to cause a comparable effect. Conversely Petrosyan[90] has shown that under-cooled austenite may be stabilized by interruption of cooling in the martensite range; when cooling is resumed after such an arrest, decomposition of austenite to martensite recommences only after a considerable temperature lag.

Valuable information for guidance in heat treatment is provided by the atlas of the transformation diagrams[91] of the main types of wrought steel in current use in Great Britain. This was prepared by a group, formed by the Thermal Treatment Sub-Committee of B.I.S.R.A., to study isothermal transformation.

The binary systems iron–carbon and iron–nitrogen and the ternary system iron–carbon–nitrogen have been studied in detail by Jack.[92] The structures of Fe_4N and Fe_2N have been established and a new iron carbide, produced by treatment of iron nitrides with carbon monoxide, has been isolated. This new carbide, known as iron percarbide, contains 31% (atomic) of carbon. A series of new ternary interstitial alloys containing iron, carbon and nitrogen (iron carbonitrides), has also been characterized by X-ray and chemical investigation. Dijkstra[93] has shown that precipitation of nitrogen from α-iron occurs in two stages, with initial formation of a precipitate of unknown composition followed by precipitation of Fe_4N. Plastic deformation both accelerates the precipitation of iron nitride and lowers the solution concentration of nitrogen in equilibrium with the precipitate.

A number of other interesting contributions have added materially to the existing knowledge of various alloy systems. The transformations occurring in binary iron–nickel and –manganese alloys during heating and cooling have been studied by Jones and Pumphrey,[94] in order to provide information on the thermodynamic properties of these systems, and Owen and Liu[95] have collected X-ray data relevant to the iron–nickel system. Teitel and Cohen[96] have obtained much of the data required to construct the beryllium–iron diagram and Bradley[97] has published the first part of an investigation designed to give a satisfactory equilibrium diagram for the iron–nickel–aluminium system. The very important series of iron–nickel–chromium alloys has been studied by Rees, Burns and Cook,[98] with particular reference to the sigma constituent, which was found to persist as an equilibrium component, after annealing, in alloys of much lower chromium content than had previously been supposed.

An interesting new technique for the isolation and examination *in situ* of non-metallic inclusions has been developed by Benedicks and Tenow.[99] A very thin specimen, about 0·02 mm. thick, is cut from the steel, mounted on a glass slide and treated with an alcoholic solution of bromine to dissolve away the steel and leave the non-metallic inclusions in their original positions and ready for microscopic examination. The carbides occurring in alloy steels have been studied in considerable detail by Koch and Wiester[100] after isolation by an electrolytic method described by Klinger and Koch.[101]

Corrosion and surface treatment

The general category of 'industrial waters' provides a wide range of corrosive conditions to which iron and steel are regularly subjected and consequently a vast amount of work on the causes and prevention of corrosion in such media has been carried out. This work has recently been comprehensively reviewed and summarized by the Corrosion Committee of B.I.S.R.A. in a Special Report[102] of the Iron and Steel Institute, which gives valuable guidance on all aspects of the prevention of corrosion by industrial waters, including choice of iron or steel of suitable composition, treatment of the water, mechanical and chemical treatment of the steel surface, use of protective coatings and other means such as cathodic protection.

Soil is another common source of corrosion and it is therefore important to know the types of steel composition which are most resistant to this form of attack. A recent investigation[103] in which steels of different compositions were tested in various types of soil showed that copper–molybdenum steels were very little better than mild steel in this respect, but that copper–nickel steels were definitely superior in all soils. Somewhat surprisingly, it was found that chromium steels did not provide good resistance to soil corrosion; although increase in chromium content was associated with decreased over-all loss in weight of the specimen, the corrosion which did occur, especially when the chromium content exceeded 6%, was localized and resulted in severe pitting which in some cases was worse than that occurring in mild steel.

An important method of minimizing corrosion in industrial waters and other media is to use some form of corrosion inhibitor, but as pointed out by Evans, in his foreword to a paper by Palmer,[104] neither anodic nor cathodic inhibitors, into which two categories most of the inhibitors in current use may be divided, are entirely satisfactory. Cathodic inhibitors do not become effective until after considerable attack has occurred, but they have the advantage of causing no deleterious effect if added in insufficient quantity. Anodic inhibitors, on the other hand, provided that sufficient is used, are in general more efficient than the cathodic type, but if too little is used, severe localized attack may occur, causing more damage than if no inhibitor had been added. Since the amount of inhibitor required depends upon a number of variables, and cannot with any certainty be specified in any given case, this provides a serious drawback to the use of anodic inhibitors. In general, anodic inhibitors operate by precipitating iron as a protective film on the metal surface, and it is believed that the localized attack, which occurs when too little inhibitor

is used, results from the formation of loose blister-like membranes which prevent access of inhibitor to the points where it is required. To overcome this difficulty, Palmer (*loc. cit.*) has experimented with inhibitors consisting of a phosphate together with an oxidizing agent (chromate or dichromate) so that the iron is precipitated as ferric phosphate which does not form a membrane, rather than as ferrous phosphate which forms the typical undesirable membranous type of precipitate. Provided that the phosphate and oxidizing agent were present in the correct ratio, this type of inhibitor was found to be efficient over a wide range of conditions and no intensified pitting resulted from a deficiency of inhibitor, but serious attack was liable to occur if phosphate and oxidizing agent were used in the wrong proportions.

Concluding his foreword, Evans expresses the view that, although this investigation has not entirely solved the problem of providing an inhibitor which is both safe and efficient for all industrial purposes, it does provide a definite step forward.

The polar organic type of inhibitor is also being increasingly used, particularly as an addition to lubricating oils to enable them to afford protection to iron and steel surfaces subjected to corrosive conditions. The theory and practice of this type of inhibitive action is considered in some detail by Baker and Zisman,[105] with particular reference to the part played by adsorption of inhibitor molecules to provide a protective coating. The mechanism of the adsorption of inhibitor molecules on metal surfaces has been studied also by Hackerman and Schmidt,[106] who show that both chemical and physical forces contribute towards the bonding of inhibitor molecules to the metal surface. It is considered that ideal inhibitive action would result from covering the entire metal surface with inhibitor molecules held by chemical forces; this would decrease the activity of each of the surface metal atoms and hinder access of the corrosive agent to the surface, and the inhibitor would not readily be dissolved in the surrounding liquid. In practice it is impossible to cover the entire surface with such 'chemisorbed' molecules but the more active parts of the surface are covered in this way, whereas the remainder of the surface is covered by physically adsorbed molecules. It should be noted that certain organic substances that are strongly chemisorbed on steel surfaces may themselves be corrosive: examples are the lower members of the fatty acid series.

Sprayed metal coatings occupy a position of increasing importance among protective coatings applied to steel. In a review of the subject by Wakefield,[107] it is pointed out that because of the almost inevitable porosity of sprayed metal coatings it is essential that they should be anodic to the base metal; zinc and aluminium therefore provide suitable coatings for the protection of iron and steel. The porosity of sprayed coatings is actually advantageous in surfaces which must be lubricated because irregularities in the surface are able to accommodate particles of metal displaced during wearing-in and the pores are able to absorb and hold an appreciable quantity of oil with consequent improvement in lubrication efficiency. New materials recently used for metal spraying[108] include an aluminium–iron–bronze, of which the wear-resistance and strength approach those of cast iron, and a molybdenum alloy which

bonds satisfactorily on any clean metal surface except copper, and so provides a suitable base upon which other metals can be sprayed. The use of metal spraying for the restoration of iron bearings and journals and for the rectification of undersized machined parts in described by Smith,[109] who emphasizes the necessity for correct surface treatment before spraying to give the required surface roughness. The various methods available for surface preparation before metal spraying are reviewed by Mansell.[110]

The electrochemical mechanism of the protective action of sprayed aluminium coatings on steel has been studied in detail by Tolley,[111] who begins by disputing the generalization that the protective action of the aluminium results from its anodic relationship to the steel base, since it has been shown that under certain circumstances the aluminium is cathodic to the steel. As the result of investigation in a variety of solutions it was found that sprayed aluminium was initially anodic to steel only in solutions of p_H lower than 3, in fairly concentrated sodium chloride solutions and in solutions containing an appreciable concentration of aluminium ions. In the other solutions, however, where the aluminium was initially cathodic it was found that on prolonged exposure the e.m.f. changed progressively in the direction of establishing aluminium as the anodic member of the couple. It is concluded that in most cases this will ultimately lead to a reversal of the potential, and the aluminium will become capable of sacrificially protecting the steel.

Another aspect of the protection afforded by sprayed aluminium coatings, also studied by Tolley,[112] is the effect on corrosion rate in sulphur dioxide atmospheres. It is shown that the rate of metallic corrosion in sulphur dioxide depends to a great extent upon the rate of catalytic oxidation of the sulphur dioxide on the metal surface. In the case of steel this is markedly decreased by spraying with aluminium.

It is shown by Wormwell and Brasher[113] that valuable information on the corrosion resistance, to marine conditions, of painted steel surfaces is provided by measurement of changes of electrode potential in synthetic sea-water. It is emphasized that measurements of potential, during the first two days of immersion, may be completely misleading as a guide to the protective value of the paint. The changes in potential must be measured over much longer periods, when it is found that the general shape of the potential–time curve shows an initial decline, followed by an increase to a maximum value, and finally a gradual decline to more negative values. The useful life of the paint under the conditions studied is the time required to pass the maximum potential.

Existing knowledge of the behaviour of 18–8 stainless steel, with particular regard to carbide precipitation and intergranular corrosion, has been reviewed by Gillett,[114] who concludes that in order to be completely immune from this form of attack, the steel would have to be lower in both carbon and nitrogen than is practicable on the commercial scale. Carbon and nitrogen contents commercially obtainable should however be sufficiently low to prevent the steel from being susceptible to intergranular corrosion after welding. Some useful quantitative data on this subject have been provided by Binder, Brown and Franks[115]; from a study of chromium-nickel steels over the range of compositions Cr 16–25%, Ni 6·5–25%, C 0·005–0·05%, N_2 0·002–0·15% (with and

without additions of niobium and molybdenum), they show that to obtain complete immunity from intergranular corrosion the carbon content must be below 0·015–0·020% depending on other composition factors. Up to 0·03% carbon, partial immunity may be given by a suitably balanced composition, whereas at carbon contents of this order a small addition of niobium confers complete immunity.

References

[1] Vaill, R., *Iron Age*, 1948, **162** (Dec. 16), 81; (Dec. 23), 64; (Dec. 30), 34
[2] Santos, T. D. de Souza, *Mineraçao e Metalurgia*, 1947, **12**, 157
[3] De Moraes, L. J., ibid., 163
[4] Lund, W., *J. Iron Steel Inst.*, 1949, **162**, 1
[5] Howard, J. J., *Iron Age*, 1949, **163** (15), 70
[6] Am. Inst. Min. Met. Eng., Blast Furnace, Coke Oven and Raw Materials Committee, 1948 Proceedings, pp. 83–126
[7] *Instituto del Hierro y de Acero*, 1948, **1**, Oct.–Dec., 50
[8] Bishop, T., *Iron Coal Tr. Rev.*, 1949, **158** (Mar. 4), 457
[9] Deans, T., *Bull. imp. Inst., London*, 1948, **46**, 104
[10] CIOS Report No. XXXII/119, Appendix 6
[11] Chesters, J. H. and Elliot, G. D., *Iron Age*, 1949, **164** (7), 89
[12] Saunders, H. L. and Wild, R., *J. Iron Steel Inst.*, 1949, **163**, 61
[13] Saunders, H. L., Butler, G. B. and Tweedy, J. M., ibid., 173
[14] Lowry, H. H., *Ind. Eng. Chem.*, 1949, **41**, 502
[15] Hatch, G. G. and Chipman, J., *J. Metals*, 1949, **1**, 274
[16] Oelsen, W. and Maetz, H., *Arch. Eisenhüttenw.*, 1949, **20**, 53
[17] Korobova, M. I. and Korobov, N. I., *Bull. Acad. Sci., U.S.S.R., Classe des Sciences Techniques*, **1946**, 567
[18] Boissin, *Rev. Industr. min.*, **1949**, 549
[19] Herzog, E., *Rev. Métall.*, 1948, **45**, 215
[20] Woods, S. E., Faraday Society, General Discussion on the Physical Chemistry of Process Metallurgy, 1948, Sept., 184, preprint
[21] Juliard, A., Rayet, R. and Ludé, A., ibid., 193
[22] Voice, E. W., *J. Iron Steel Inst.*, 1949, **163**, 312
[23] Bishop, T. and Lewis, K. G., *Iron Coal Tr. Rev.*, 1948, **157**, 1349, 1403
[24] Newell, W. C., Langner, A. J. and Parsons, J. W., *Inst. Brit. Foundrym. Pap.*, June 1948, No. 908
[25] Brunt, F. and Parnham, H., *Iron Coal Tr. Rev.*, 1949, **159**, 631
[26] Newby, M. P., *J. Iron Steel Inst.*, 1949, **162**, 452
[27] Caine, J. B., *Amer. Foundryman*, 1949, **15** (Mar.), 46
[28] Colditz, P. von, ibid., 1948, **14**, 38
[29] Morrogh, H. and Williams, W. J., *J. Iron Steel Inst.*, 1948, **158**, 306
[30] Donoho, C. K., *Amer. Foundryman*, 1949, **16** (Jul.), 36
[31] De Sy, A., ibid., **15** (Jan.), 55
[32] Donoho, C. K., ibid. (Feb.), 30
[33] Reese, D. J., ibid., **16** (Jul.), 32
[34] Mardon, H. H. and Terrington, J. S., *J. Iron Steel Inst.*, 1949, **161**, 327
[35] Jackson, A., ibid., **162**, 136
[36] *Iron Coal Tr. Rev.*, 1949, **159** (Sep. 30), 92
[37] Ibid., 42
[38] *Iron & Steel*, 1949, **22** (Feb.), 49
[39] Chesters, J. H. and Thring, M. W., Iron and Steel Institute, 1946, Special Report, No. 37
[40] Chesters, J. H. and Philip, A. R., *J. Iron Steel Inst.*, 1949, **162**, 385
[41] Howes, R. S. and Philip, A. R., ibid., 392
[42] Halliday, I. M. D. and Philip, A. R., ibid., 401
[43] Collins, R. D. and Tyler, J. D., ibid., 457
[44] Thring, M. W., *Iron Coal Tr. Rev.*, 1948, **157** (Nov. 12), 1063
[45] Carlisle, S. S. and Smith, B. O., *J. Iron Steel Inst.*, 1949, **161**, 222
[46] Robertson, F. L. and Thring, M. W., ibid., **163**, 31
[47] Diamond, E. L. and Frankau, A. M., ibid., **161**, 191

[48] Gumpp, F. W., *Iron Steel Engr*, 1949, **26** (Jan.), 126
[49] Short, C. W. and Meyrick, T. G., *Iron Coal Tr. Rev.*, 1948, **157** (Oct. 1), 725
[50] Berner, L. R., Amer. Inst. min. metall. Engrs., Proc. 31st Nat. Open Hearth Conference, April, 1948, 232
[51] Warren, H. E., *ibid.*, 236
[52] Maddocks, W. R. and Turkdogan, E. T., *J. Iron Steel Inst.*, 1949, **162**, 249
[53] Ibid., 57
[54] Eisaman, J. H., Amer. Iron and Steel Inst., 1948, May, preprint
[55] Iron and Steel Inst., 1949, Special Report, No. 42
[56] Graham, H. W., *Steel*, 1949, **124** (Apr. 11), 90; (Apr. 18), 114; (Apr. 25), 102
[57] Bain, E. C. and Graham, H. W., *Iron Age*, 1949, **163** (Apr. 7), 62
[58] Warchol, J. A., *Blast Furn.*, 1948, **36** (Dec.), 1461, 1469
[59] Binnie, D., *J. Iron Steel Inst.*, 1949, **163**, 159
[60] Chipman, J., Faraday Society, General Discussion on the Physical Chemistry of Process Metallurgy, Sept. 23, 1948, 23
[61] Chipman, J., *Metal Progr.*, 1949, **56** (2), 211
[62] Kitchener, J. A., Bockris, J. O'M and Liberman, A., Faraday Society, General Discussion on the Physical Chemistry of Process Metallurgy, Sept. 23, 1948, 49
[63] Carter, P. T., *ibid.*, 307
[64] Herasymenko, P., *Trans. Faraday Soc.*, 1938, **34**, 1245
[65] Guggenheim, E. A., Faraday Society, General Discussion on the Physical Chemistry of Process Metallurgy, Sept. 23, 1948, 317
[66] Carter, P. T., *ibid.*, 326
[67] Bockris, J. O'M., Kitchener, J. A., Ignatowicz, S. and Tomlinson, J. W., *ibid.*, 265
[68] Richardson, F. D., *ibid.*, 244
[69] Chipman, J. and Chang, Lo-Ching, *J. Metals*, 1949, **1**, 191
[70] McCance, A., *J. Iron Steel Inst.*, 1949, **163**, 241
[71] Wilms, G. R. and Wood, W. A., *J. Inst. Met.*, 1949, **75**, 693
[72] Mott, N. F., *Research*, 1949, **2**, 162
[73] Digges, T. G., Irish, C. R. and Carwile, N. L., *J. Res. nat. Bur. Stand.*, 1948, **41**, 545
[74] Comstock, G. F., *Iron Age*, 1949, **163** (June 16), 90
[75] Bardgett, W. E. and Reeve, L., *J. Iron Steel Inst.*, 1949, **163**, 277
[76] Krynitsky, A. I. and Stern, H., *J. Res. nat. Bur. Stand.*, 1949, **42**, 465
[77] Micksch, J. E., Fabert, H. A. and Cover, G. M., *Amer. Foundryman*, 1948, **14** (Aug.), 30
[78] Stewart, W. C. and Williams, W. L., *J. Amer. Soc. naval Engrs*, 1948, **60** (Nov.), 475
[79] Eugène, F., *Rev. Métall.*, 1949, **46**, 193
[80] Sims, C. E., Moore, G. A. and Williams, D. W., *Amer. Inst. min. metall. Engrs, Met. Technol.*, T.P. No. 2454, 1948, **15**
[81] Bastien, P. and Azou, P., *C.R. Acad. Sci., Paris*, 1949, **228**, 1651
[82] Merriman, A. D., *Metallurgia, Manchr.*, 1949, **39**, 139
[83] Scherzer, O., *J. appl. Phys.*, 1949, **20**, 20
[84] Cuckow, F. W., *J. Iron Steel Inst.*, 1949, **161**, 1
[85] Forgeng, W. D., *Iron Age*, 1948, **162** (Oct. 14), 130
[86] Rollason, E. C., Sharratt, E. and Roberts, R. R., *J. Iron Steel Inst.*, 1949, **162**, 265
[87] Kurdyumov, G. V. and Maksimova, O. P., *C.R. Acad. Sci. U.R.S.S.*, 1948, **61**, 83
[88] Thompson, F. C. and Jepson, M. D., *J. Iron Steel Inst.*, 1950, **164**, 27
[89] Jepson, M. D. and Thompson, F. C., ibid., 1949, **162**, 49
[90] Petrosyan, P. P., *C.R. Acad. Sci. U.R.S.S.*, 1948, **59**, 1109
[91] Iron and Steel Inst., 1949, Special Report, No. 40
[92] Jack, K. H., *Proc. roy. Soc.*, 1948 [A], **195**, 34
[93] Dijkstra, L. J., *J. Metals*, 1949, **1**, 252
[94] Jones, F. W. and Pumphrey, W. I., *J. Iron Steel Inst.*, 1949, **163**, 121
[95] Owen, E. A. and Liu, Y. H., ibid., 132
[96] Teitel, R. J. and Cohen, M., *J. Metals*, 1949, **1**, 285
[97] Bradley, A. J., *J. Iron Steel Inst.*, 1949, **163**, 19
[98] Rees, W. P., Burns, B. D. and Cook, A. J., ibid., **162**, 325
[99] Benedicks, C. and Tenow, O., ibid., **161**, 177
[100] Koch, W. and Wiester, H. J., *Stahl. u. Eisen, Düsseldorf*, 1949, **69**, 73
[101] Klinger, P. and Koch, W., ibid., 1948, **68**, 321

[102] Iron and Steel Inst., 1949, Special Report No. 41
[103] American Gas Association, 'Industrial Finishing,' 1949, pp. 362–365
[104] Palmer, W. G., *J. Iron Steel Inst.*, 1949, **163**, 421
[105] Baker, H. R. and Zisman, W. A., *Ind. Eng. Chem.*, 1948, **40**, 2338
[106] Hackerman. N. and Schmidt, H. R., *Corrosion*, 1949, **5**, 237
[107] Wakefield, J. E., *Metal Progr.*, 1948, **54**, 827
[108] Idem., *Iron Age*, 1949, **163** (Mar. 17), 81
[109] Smith, K. B., *Welding J.*, 1949, **27**, 941
[110] Mansell, R., *Steel Processing*, 1949, **35**, 241
[111] Tolley, G., *J. Iron Steel Inst.*, 1949, **162**, 377
[112] Idem, *J. Soc. chem. Ind.*, 1948, **67**, 369, 401
[113] Wormwell, F. and Brasher, D. M., *J. Iron Steel Inst.*, 1949, **162**, 129
[114] Gillett, H. W., Amer. Soc. Testing Materials, 1949, Preprint No. 22
[115] Binder, W. O., Brown, C. M. and Franks, R., Amer. Soc. for Metals, Oct. 1948, Preprint No. 25

NON-FERROUS METALS

PHYSICAL METALLURGY (D. W. Wakeman, B.Sc., Ph.D.)

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A NUMBER of reviews appeared during the year, notably the series of FIAT Reviews of German Science, 1939–1946,[1] which contain much information on non-ferrous metals. A book[2] edited by Professor B. Chalmers, which contains a series of reviews of various topics in the field of physical metallurgy, has been published.

Physical properties

Deformation of metals.—The year has been productive of many theoretical papers on the plastic behaviour of metals, both the 'classical' type of plasticity theory which considers the macroscopic behaviour only, and the type of theory which postulates some structural mechanism of flow. To the first group belong such papers as those of Prager,[3] Epstein,[4] and Hill[5] who considers the strain of anisotropic metals. In the second group a wide range of points of view, not necessarily contradictory, is shown. Slip on slip bands has been considered as a process of nucleation and growth.[6,7] Stress–strain relationships have been discussed in terms of the general statistical rate theory of chemical and physical processes.[8] As a particular example, a stress–strain relationship for constant rate of strain is developed. McCance[9] discusses a theory which assumes that in a metal under stress a proportion θ of the atoms are in a distorted lattice characteristic of cold-worked material, the remainder being in a regular lattice. By consideration of the dimensional changes occuring when $\delta\theta$ atoms change from a regular to a distorted lattice he obtains a relationship between stress and strain for a metal. The theory of dislocations, considered as the elementary process of slip, has been further developed by a number of workers. Nabarro[10] has reviewed British contributions to dislocation theory. Mott[11] has given a general review of the present state of dislocation theory. Dean and Mann[12] have given a detailed mathematical treatment of the strain energy surrounding a dislocation. Bragg[13] has used this treatment to derive expressions for the yield stress of a cold-worked metal. By using results from X-ray line-broadening experiments he has estimated the ultimate shear strength of several metals, obtaining values in fair agreement with experiment. Many discussions of dislocations have assumed an isotropic material and crystals of cubic symmetry. Eshelby[14] has obtained general formulæ for edge-type dislocations in anisotropic materials in which the lattice symmetry is that of any of the crystal classes. As an example of the application of these formulae Eshelby has shown that dislocations of such a type that the slip plane is (110) and the slip direction (111) in α-iron, should move more readily under an applied shear stress than other types of dislocation. Cottrell's theory that solute atoms which strain a crystal lattice migrate to the distorted lattice regions round a dislocation to form 'atmospheres' has been further developed.[15] The existence of

such atmospheres makes it possible to consider two types of moving dislocation: slow dislocations accompanied by partially formed atmospheres, whose speed is limited by the rate of migration of the solute atoms; and fast dislocations whose speeds may approach that of the velocity of sound in the metal, too great a speed for a solute atmosphere to form round them. Cottrell and Jaswon's paper considers this first type of slow dislocation, and shows that the presence of the solute-atom atmosphere round the moving dislocation exerts a force on the dislocation, increasing linearly with the speed of the dislocation up to a critical range, above which the dislocation accelerates away from its solute-atom atmosphere. The characteristics of the plastic flow below this critical range can be compared with those of microcreep in tin single crystals at room temperature, and quite close agreement is found. They conclude that the type of creep expected from the movement of slow dislocations closely resembles microcreep; before a critical comparison of theory and experiment can be made, however, a better knowledge of the dependence of microcreep on temperature, and of the diffusion rates of specific solute elements in tin is necessary.

Bragg and Lomer in a series of papers[16,17,18] have described the properties of a two-dimensional raft of bubbles on the surface of a liquid. The plastic properties of such a raft show many analogies to those of a metal. They point out that the analogy is by no means perfect, particularly when quantitative comparisons are made, but it has many interesting qualitative features, which may be significant and suggestive for the theories of the plastic behaviour of metals. For example, dislocations similar to the type originally suggested by Taylor occur in the bubble raft; those already present move under very small shear stresses, whereas the formation of dislocations in an originally perfect raft occurs only at quite large shear stresses.

Single crystals.—A number of papers describing experimental work with single metallic crystals has appeared during the year. Heidenreich[19] has described a method for the preparation of very thin, undistorted metal crystals suitable for examination by electron microscopy; he considers that such thin sections may offer a method of investigating dislocations, though a detailed examination of images obtained from such a study has not yet been made. Another interesting paper using electron microscope techniques is by Brown[20] who shows that slip-bands in aluminium consist of groups of glide lamellae 200–800 A. thick which have slipped over each other by 1600–2000 A. Variation of the temperature, type, and rate of deformation does not alter the slip unit, but only their grouping into clusters which form the slip band.

Gwathney[21] and Holden[22] have reviewed methods of preparation of single crystals, and Tiedema[23] has described a method of preparation of aluminium single-crystal plates or wires having any desired orientation to within 1°. Cottrell and Gibbons[24] have shown that single crystals of cadmium prepared in nitrogen, or in argon contaminated with a little nitrogen, show a yield point analogous to that in mild steel. This analogy is discussed in relation to Cottrell's conception mentioned above of a dislocation surrounded by an atmosphere of solute atoms; the yield point is associated with the force necessary to tear the dislocation away

from its atmosphere to form a fast dislocation. Creep experiments on single-crystal cadmium wires have been described by Andrade and Randall.[25] Wires heated for 30 min. at 200° c. before creep testing showed no thermal hardening; a 20-hr. treatment produced hardening, reducing the creep rate, as heating a specimen contaminated with cadmium nitrate for 30 min. at 200° c. did. Surrounding a wire by a commercial cadmium plating solution during testing was found to increase the rate of creep as much as 20-fold. The increase in the rate of flow was attributed to the surface effects of cadmium ions. Hardening effects were considered to be due to surface film formation. Holden and Holloman[26] were unable to show a yield point in single crystals of iron, whether decarburized, carburized, or nitrided. A yield point was found in polycrystalline iron specimens when carburized or nitrided, but not when decarburized. These experiments indicate that the yield point is associated with grain boundary effects as against Cottrell's explanation of the yield point. In direct opposition to this work, other workers[27] have demonstrated the existence of a yield point in single crystals of iron containing small amounts of nitrogen or carbon; further experimental evidence on this point appears desirable. Cahn[28] has described a special type of recrystallization, called 'polygonization,' in bent single crystals after annealing. The crystal becomes a series of lamellae, each orientated at a small angle of a few minutes of arc from its neighbours. A similar phenomenon in aluminium single crystals has been described by Guinier and Lacombe.[29]

Internal friction.—The measurement of internal friction and damping capacity has been a fruitful field of research. Eshelby[30] has discussed an interesting correlation between the internal friction of single crystals and dislocation theory. He suggests that dislocations may be trapped in 'potential troughs' at the minima of internal stresses in the metal. When the crystal vibrates the dislocations vibrate in their potential troughs, and the moving stress system associated with this movement produces a fluctuating temperature distribution in the material, leading to damping. There are indications, however, that this source of loss may in many cases be small compared with other sources of damping in single crystals.

Potter[31] and Boulanger[32] have reviewed methods of measurement of internal friction. The elastic properties and internal friction of single crystals of aluminium,[33,34] nickel,[35] and zinc[36] have been measured. The internal friction of metals containing small amounts of other elements in solid solution is the subject of a number of papers. Zener[37] has given a general discussion of the problem; he considers in particular carbon- and nitrogen-bearing iron, in which the solute element is in interstitial solid solution. The solute atoms in the presence of stress show a preferred distribution among the various types of interstitial position in the lattice; an oscillating stress causes a continually changing distribution of solute atoms, and this effect is shown to cause peaks in the internal friction–frequency spectrum. Koehler[38] has considered the damping associated with the movement of dislocations anchored by impurity atoms in the manner proposed by Cottrell. Damping at frequencies of a few kilocycles per second is shown to be inversely proportional to the

square of the concentration of impurities. This gives a good explanation of the large effect of traces of hydrogen on the damping of copper.

Experimental work by Kê[39] on the internal friction of tantalum containing nitrogen in interstitial solid solution has been interpreted as showing that the nitrogen atoms are situated at both the octahedral and the tetrahedral interstices in the tantalum crystal lattice. As in Zener's discussion of carbon and nitrogen in iron, stress was considered to cause a preferential distribution of solute atoms amongst the lattice interstices. The precipitation of nitrogen from solid solution in iron has been studied by both damping capacity measurements and by micrographic methods.[40] The results suggested two successive stages in precipitation: first a precipitation of plates of unknown lattice structure on the (100) lattice planes, then the compound Fe_4N forms.

Creep.—The creep of metals under constant stress is usually considered to consist of two or three stages : the first stage during which the creep rate, initially high, decelerates ; a second, steady, state in which the creep rate is constant ; and in some cases a final stage in which the creep rate increases. An elegant theory of the initial or transient creep stage has been put forward by C. L. Smith.[41] He assumes that the metal contains dislocations 'trapped' at the minima of internal stresses in the metal. These dislocations can be released by thermal fluctuations and move under the applied stress, giving the resultant strain of the specimen. The transient character of the creep is ascribed to the progressive exhaustion of dislocations requiring low activation-energies for release. The relationship $\epsilon = \text{constant} \times T(1 - e^{-Ct})/t$ is deduced connecting the creep strain ϵ, the absolute temperature T, and the time t ; C is a constant. Reasonable agreement was obtained with experiments on the creep of single-crystal specimens of zinc, lead, and copper. The X-ray and micrographic work of Wood and others[42] on the deformation and creep of polycrystalline metals has laid emphasis on the break up of the grains by deformation into crystallites of differing orientation, and they discuss the relationship between this crystallite formation and steady-state creep.

Recrystallization.—Other evidence in support of a substructure in the individual grains of recrystallized metals has been given by the careful micrographic work of Lacombe *et al.*[43,44] ; their work on annealed, very pure aluminium and aluminium–zinc alloys indicates a substructure of blocks within each crystal, of a size visible under the microscope, very slightly disorientated with respect to each other. A review of this topic[45] discusses the evidence for this type of substructure, and for a submicroscopic mosaic structure of the type considered by Wood.

Large crystals, prepared by recrystallization after critical cold working, frequently show small crystals as inclusions which resist absorption even after prolonged annealing.[46,47] It has been shown that two main types of small inclusion occur : in the first type the inclusion has a twin relationship, correct to within a few degrees, to the surrounding large crystal ; it is considered that this is a grain of the original unrecrystallized material which accidentally possessed an approximately twin orientation, was thus difficult to absorb, and remained unconsumed. In the second type of inclusion the twin orientation is exact, and the inclusion is considered to have grown from a nucleus within the larger grain by stimulation.

An observation which shows some analogy with the first type of inclusion has been made by Beck and Sperry[48] who show that grain growth in recrystallized aluminium is greatly retarded when the structure has marked preferred orientation.

Continued interest is shown in the phenomena of recrystallization after cold work, and grain growth. Burgers[49] has given a general theoretical discussion of the subject, considering both the mathematical treatment of nucleation and growth and the separate problem of the actual atomic mechanism. He suggests that the atomic mechanism is one in which a mosaic lattice block in the deformed matrix may be induced to grow by the dissolution of a number of dislocations of opposite sign, thus creating a stress capable of moving one of its boundaries. This process would usually be activated by thermal fluctuations. Burgers considers the orientation relationships which occur in recrystallization, and emphasizes that a comprehensive theory which would include an explanation of such relationships is still needed. An empirical formula for grain growth in pure metals and some solid solutions has been given by Beck.[50] Papers have appeared on the recrystallization after cold work of aluminium,[51,52] copper,[53] zinc and zinc alloys,[54] and beryllium.[55,56]

Diffusion.—Radioactive isotopes of a number of metals are becoming increasingly available, and use has been made of these to determine coefficients of diffusion and self-diffusion. The rate of self-diffusion in single crystals and in polycrystalline specimens of silver has been measured.[57] The apparent self-diffusion coefficient in the polycrystalline specimens was higher and the activation energy of diffusion was lower than in the single crystal specimens, indicating a marked grain boundary effect. Work on the diffusion of silver in copper[58] also indicates that the activation energy for grain boundary diffusion is lower than that for volume diffusion, and it was shown that the rate of diffusion is dependent on the relative orientation of the grains forming the boundary. The theory of diffusion has been discussed by Seitz[59] on the basis of the migration of lattice vacancies. He considers various possible interatomic processes for diffusion but suggests that the experimental data can only be fully explained in terms of processes more complex than those usually considered.

Properties of alloys

A review of recent advances in the study of the crystalline state by Bragg[60] is of much general interest; among other matters he discusses the investigations of the groups of workers under Hume-Rothery and Raynor on alloy constitution and theory; he also discusses order–disorder transformations and precipitation in solid alloys.

Alloy constitution.—A very large number of investigations on alloy constitution and associated topics has been reported in the literature during the year. Pauling, in his work on the electron structure of metals, has always taken a different point of view from that typified, for example, by Mott and Jones' book "The Properties of Metals and Alloys." His recent papers[61] discuss further developments of his resonating valence bond theory, and this theory appears to give a useful alternative explanation for a number of the structural properties of alloys, particularly for

the transitional metals. Pauling discusses the relationship between his theory and the more usual bond theory and shows that the existence of Brillouin zones is compatible with his ideas.

Hume-Rothery[62] has reviewed the problem of the comparison of the sizes of atoms in different metallic structures. Starting with his original concept that an approximate measure of the size of an atom of a metal is the interatomic distance in the crystal of the element, he shows that this distance is affected by change in co-ordination number and by Brillouin zone effects. He defines an 'apparent atomic diameter' of a solute element in solid solution in a metal: this is the value obtained by extrapolating to 100% solute the tangent of the lattice spacing curve at zero solute concentration. This value for a given solute element varies with different solvents, and he shows that an important factor is the volume per valency electron in the elements concerned. If this volume is larger for solute than solvent, the apparent atomic diameter of the solute tends to be small compared with the atomic diameter in the pure solute metal; if this volume is smaller for solute than solvent the apparent diameter tends to be large. Hume-Rothery has also shown an empirical correlation between interatomic distances in the crystals of certain elements and their atomic numbers; in particular there appears to be a linear relationship between the square of the interatomic distance at absolute zero and the atomic number in certain of the groups of the Periodic Table.[63]

Raynor has suggested, on the basis of Pauling's earlier theory, that the transitional metals when present in a structure of high electron : atom ratio absorb electrons from the structure as a whole, so that, for example, iron, cobalt, and nickel absorb 2·66, 1·71 and 0·61 electrons per atom respectively. Further evidence for this concept has been given in papers published recently. Since two atoms of cobalt will absorb approximately the same number of electrons as one atom of iron plus one atom of nickel, and other properties of the three types of atom are similar, it was suggested that the equilibrium diagram for aluminium-rich alloys of the ternary system aluminium–iron–nickel should be almost identical with a pseudo-ternary diagram made up by placing together the ternary diagrams for aluminium-rich alloys of the systems aluminium–iron–cobalt and aluminium–cobalt–nickel. The equilibria in the systems aluminium–iron–nickel and aluminium–cobalt–nickel were already known; on the basis of the above concept the nature of the system aluminium–iron–cobalt was predicted. This latter system has now been investigated experimentally[64] and remarkably close agreement between experiment and prediction was found. Further evidence of the absorption of electrons by cobalt when alloyed with aluminium is given by a careful *X*-ray investigation of the crystal structure of Co_2Al_9.[65] A Fourier synthesis of the structure indicated that the number of electrons within the cobalt peak was approximately two more than the normal 27; this is direct evidence of electron absorption. Probable Brillouin zones for the phases Co_2Al_9 and $NiAl_3$ have been deduced[66] and these zones are characterized by inscribed Fermi spheres which can contain numbers of electrons per atom in close agreement with electron : atom ratios calculated for these phases on the basis of Raynor's concept. The system aluminium–cobalt–copper has been investigated.[67] It contains a ternary compound whose

composition range was not determined exactly but is very probably based on the formula $Co_2Cu_5Al_{13}$. This is analogous to the compounds $NiCu_3Al_6$ and $FeCu_2Al_7$, and has the same electron : atom ratio, 2·04, when calculated on the basis of Raynor's concept.

Two silver-rich ternary systems, silver–magnesium–tin[68] and silver–magnesium–zinc,[69] have been investigated. The form of the equilibria are discussed in terms of general alloy theory with particular reference to size-factor, electron : atom ratio, and the free energy of formation of the phases. For details of this very interesting discussion, however, the original papers should be consulted. Aluminium–magnesium–zinc is another alloy system discussed in terms of alloy theory.[70]

The primary solid solubility boundary for silver in aluminium has been redetermined.[71] The boundary shows a marked inflexion at 49·4% silver and 526° C., this composition representing the same electron : atom ratio as the peak of the $(\alpha + \alpha_1)$ miscibility gap in the system aluminium–zinc. This indicates an electronic factor in both systems tending to cause a separation of the solid solution into two phases at this electron : atom ratio. In the aluminium–silver system the solid solubility curve lies at too high a temperature for actual separation to occur. This factor is discussed in terms of the Brillouin zone for aluminium. Independently two other workers have discussed anomalies in the lattice spacing[72] and electrical resistivity[73] of aluminium–zinc alloys and related them to the Brillouin zone for aluminium.

The coefficients of thermal expansion of solid solutions of various elements in aluminium have been measured.[74] It is shown that the coefficient of expansion of aluminium is increased both by solution of elements which expand and elements which contract the lattice; the increase thus appears to be due to lattice distortion without reference to the sign of the distortion.

An interesting method of investigating certain properties of alloys has been described : that of measuring the catalytic action of such alloys on the dehydrogenation of formic acid vapour.[75] It is found that the activation energy depends on the electron concentration and lattice type of the alloys.

The constitution of aluminium–copper–magnesium alloys has been studied as part of an investigation on the constitution of aluminium-rich alloys under conditions of metastable equilibrium likely to be met with in industrial practice.[76] Other aluminium-based systems investigated include aluminium–tin,[77] aluminium–magnesium–zinc,[78] aluminium–copper–magnesium–silicon and aluminium–iron–magnesium–silicon.[79] Copper-based systems include copper–zinc–magnesium[80] and copper–nickel–aluminium.[81]

The determination of alloy constitution in systems containing high melting point metals is experimentally difficult. Despite this, a number of investigations of such systems have been reported this year: they include studies of the systems manganese–nickel,[82,83] manganese–zinc,[84] chromium–manganese,[85] platinum–tungsten,[86] and nickel-thorium.[87]

Other systems reported in the literature include: bismuth–indium[88]; beryllium–iron[89]; beryllium–gold[90]; gold–cadmium[91]; gold–silver–copper[92]; magnesium–indium[93]; lead-rich ternary systems containing

zinc and one of the elements arsenic, antimony, tin, bismuth, copper, silver, or gold[94]; lead–sodium–antimony, lead–sodium–arsenic, lead–antimony–zinc–sodium, lead–calcium–bismuth–magnesium, lead– potassium–bismuth–magnesium[95]; binary alloys of tin with various transitional metals[96]; tin–antimony–sulphur[97]; titanium–nickel[98]; zinc–chromium[99]; zinc–lead–silver, zinc–lead–copper, zinc–bismuth–silver, zinc–bismuth–copper[100], zinc–aluminium–copper[101]; binary sytems of zirconium with copper, silver, or gold.[102] A number of pseudo-binary systems between the monocarbides of high-melting-point metals have been investigated.[103,104]

Alloy structure.—In addition to studies of structure made as an integral part of the investigations in alloy systems mentioned above, a number of communications more specifically concerned with crystal structure have appeared. X-ray investigations have been made of the structures of the compounds CrB,[105] Cu_2MnIn (with reference to its ferro-magnetic properties),[106] Ni_4W,[107] and Co_7Mo_6[108]; of uranium,[109] and compounds of uranium with aluminium, mercury, and tin.[110]

The atomic reactor is a rich source of neutrons and neutron-diffraction by crystals, using such a source, can supplement the more usual X-ray and electron-diffraction techniques in the investigation of crystal structure. The theoretical and practical problems have been discussed[111]; the method has been used to investigate the constitution of tungsten and titanium carbides,[112] and order–disorder changes.[113] Neutron diffraction was particularly successful in showing an ordered structure in the compound FeCo, for which X-ray methods are difficult.

Some interest is shown in the order–disorder transformation. Borelius[114] has discussed the mechanism generally and given a relationship for free energy changes as a function of degree of order; he uses this to discuss order in CuZn and CuAu. For CuZn the ordering process proceeds continuously from full to zero order. For CuAu the process is discontinuous, and metastable states may occur; the discontinuity is related to the influence of potential barriers. Raub has shown that small additions of silver lower the critical temperatures of ordering in both CuAu and Cu_3Au, but the effect is less with Cu_3Au.[115] The process of ordering in the alloy CoPt has been shown to be discontinuous.[116] An almost linear relationship between the degree of short-range order and the lattice parameter of Cu_3Au has been demonstrated.[117] Betteridge, as a consequence, makes the interesting suggestion that the lattice parameters of solid solutions are better correlated with interatomic bond lengths than with atomic diameters, although he shows that bond length may vary with changes in electron : atom ratio.

Precipitation hardening.—The process of precipitation hardening in super-saturated solid solutions has been considered from three main points of view. The first approach tries to explain the increased resistance to deformation caused by the precipitation, to some extent this has been discussed by Mott in terms of dislocation theory.[11] The second approach considers the rate of precipitation. Borelius has discussed this in terms of the free energy–concentration curves for the solid solution. He divides the temperature–composition diagram into two areas in which the second differential of free energy as a function of composition is in one case positive, and in the other case negative. He suggests that the

solid solution at temperatures and compositions corresponding to points in the diagram for which this function is positive should show retarded precipitation. Recent experimental work on aluminium–zinc alloys is in reasonable quantitative agreement with this theory.[118] The third approach attempts to explain the structural and physical changes occurring during age-hardening in terms of a structural mechanism, which is essentially a nucleation and growth process. Processes of varying degrees of complexity have been proposed. A useful review of this type of theory has been made by Hardy.[119] The explanation is usually in terms of a three-stage process : (i) a concentration of solute atoms at various positions in the metal, (ii) these clusters changing to an intermediate type of precipitate, (iii) a precipitate with the composition and lattice-structure of the equilibrium phase forms. Processes with further intermediate steps have, however, been proposed.

The first stage has been considered by Smoluchowski.[120] Fluctuations in composition will cause strains near each group of solute atoms, affecting both the configuration and the probability of occurrence of such clusters. Smoluchowski was thus able to show, as an example, that silver in solid solution in copper will tend to cluster on the (100) planes, and the solid solution of copper in silver will lead to clusters of copper atoms on the (111) planes. Guinier,[121] discussing his own X-ray investigations, shows that the clusters in the solid solutions of zinc and silver in aluminium are spherical; this agrees with the fact that silver and zinc atoms cause very little strain to the aluminium lattice. In the solid solutions of copper in aluminium, and beryllium in copper, the clusters are plate-like. Guinier also discusses the later stages of the precipitation. Geisler[122] has reviewed the correlation between the structural process and the observed property-changes during precipitation. He emphasizes that precipitation will be accelerated in regions of high energy such as grain boundaries. Evidence has been given[123] for a form of clustering in solid solutions of silver, and of magnesium plus silicon, in aluminium, in which the initial clustering is in the form of 'stringlets' 10 by 20 A. in cross-section and over 100 A. in length. Evidence for clustering is usually obtained by X-ray investigations; electron microscope techniques can also give evidence for this clustering.[124] The change from the second to third stages of precipitation —from intermediate to final precipitate—may occur by a series of lattice-shearing processes. It has been suggested that this shear may co-operate with applied stresses and facilitate plastic deformation.[125] In an aluminium–12% zinc alloy precipitation was found experimentally to assist creep, in agreement with this concept. Precipitation in an aluminium–4% copper alloy did not affect creep; it was suggested that the structural change did not occur by shear, or else that the shear was not on the (111) planes, and so would not affect plastic deformation. The precipitation processes in Cunico (copper 50%, nickel 21%, cobalt 29%),[126] and gas turbine alloys[127] have been described.

Properties of wrought alloys

Aluminium alloys.—The effect of small additions of various elements upon the mechanical properties of pure (99·5%) aluminium has been investigated.[128] 1·1% iron, 0·2% beryllium, or 0·35% zirconium raised

the recrystallization temperature by 100–300° c. The highest tensile properties for worked material were found in alloys with 0·19% magnesium and the iron and zirconium alloys. A quarternary alloy (0·43% iron, 0·32% magnesium, 0·1% silicon) had good creep resistance combined with high electrical conductivity. Experiments to develop a high strength wrought aluminium–magnesium–zinc alloy have been described, and the effects of small amounts of other elements on the properties investigated.[129] The best tensile properties in the heat-treated and aged condition (58 kg./mm.^{2} proof stress, 70 kg./mm.^{2} ultimate tensile stress, 8% elongation) were obtained with an alloy containing 8·3% zinc, 3·7% magnesium, 0·2% chromium, 0·2% manganese and 1% copper. The effect of tin on the mechanical properties of some aluminium alloys has been investigated[77]; it was shown that small amounts of tin may raise the mechanical properties of fully heat-treated and aged aluminium-copper alloys. The hardness, tensile, impact and fatigue properties of various commercial aluminium and magnesium alloys have been investigated at temperatures down to −253° c.[130] These mechanical properties increased markedly as the temperature was lowered; ductility, particularly for magnesium alloys, was somewhat reduced. The effect of rolling and annealing procedures on the grain size and structure of aluminium–manganese–magnesium[131] and aluminium–copper–magnesium[132] alloys has been described; the age-hardening alloy 61S has been shown to develop slightly better mechanical properties after quench-ageing (i.e. quenching from solution treatment temperature into a bath held at the ageing temperature) than when water-quenched followed by artificial ageing.[133] The effect of over-ageing at temperatures from 150–400° c. in the alloy B.S.S. L42 has been investigated, with the object of deriving the operating temperatures of engine components of this alloy from hardness and micrographic examination.[134] The aluminium corner of the quarternary system aluminium-copper-magnesium–silicon at a copper content of 4% has been investigated, and the equilibria correlated with the quench-cracking of overheated Duralumin-type alloys.[135]

Copper alloys.—Cook has given a general survey of recent progress in the metallurgy of copper and its alloys.[136] The creep properties of six types of commercial copper, two containing 0·06% silver, have been investigated.[137] Cold work increased creep strength; the benefit of cold work is of course lost at temperatures at which recrystallization is rapid; the presence of silver is beneficial in reducing the creep rate by raising the temperature of recrystallization. The fatigue properties of a large range of commercial copper alloys,[138] and copper–2% beryllium alloys with small amounts of iron, cobalt, or nickel[139] have been investigated. The mechanical properties of copper–iron alloys have been studied in an attempt to produce a strong alloy of high electrical conductivity.[140] Drawn wires can be obtained with a conductivity 50% of that of pure copper and a tensile strength of about 70 tons/in.^{2}, the preferred composition being 10–15% iron and 0·03–0·1% magnesium. Samuels, on the basis of careful micrographic work, considers that the embrittlement of copper by small amounts of bismuth is not as previously suggested due to an actual film of bismuth on the grain boundaries, but by a concentration of bismuth atoms near the grain boundaries without actual

precipitation.[141] Lithium, in amounts of 0·01–0·03%, has been shown to remove embrittlement by 0·007% bismuth in copper and a number of copper alloys.[142]

Magnesium alloys.—The notch sensitivity in axial tension of a number of wrought magnesium alloys has been studied[143]; the notch sensitivity showed no direct correlation with the more usual type of tensile data. A new development in magnesium alloys which promises to have good commercial value is the magnesium–lithium alloy series.[144] The addition of 10·3% or more of lithium to magnesium changes the crystal structure from hexagonal to body-centred cubic, with a consequent improvement in formability, and rolling and extrusion characteristics. The alloys can be melted under a lithium chloride–lithium fluoride flux, and cast in air in cast iron or graphite moulds. They can be hot-worked at 230° C.; total reductions of 50% are possible in cold rolling. Alloying additions improve the properties of the binary alloys, silver being the most effective. One alloy (68·5% magnesium, 11·5% lithium, 15% cadmium, 5% silver) had a yield strength of about 21 tons/in.^{2}, and an elongation of 8%, and its properties are maintained at slightly elevated temperatures up to 65° C. for long periods. The corrosion resistance of such complex alloys are poor; the binary 11% lithium alloy has good corrosion resistance and may be used to clad the higher strength alloys. Mellor and Ridley[145] have investigated the creep strength at 200° C. of magnesium alloys containing up to 6% cerium and 1·6% manganese. In binary aluminium–cerium alloys, although small amounts of cerium increased the creep strength, more than 1·5–2% cerium had little advantage under their experimental conditions. Some slight age-hardening was found in alloys with 0·5% cerium and over, and the creep resistance appears to be associated with this. Similar results were obtained with alloys containing both cerium and manganese and the creep resistance was somewhat enhanced.

Lead alloys.—The creep of lead containing small amounts of silver, copper,[146,147] or calcium[148] has been investigated. Silver has little or no effect; copper increases creep resistance slightly; and calcium in amounts of about 0·05% markedly reduces the creep rate.

Nickel alloys.—In the investigation of a series of nickel alloys for high-temperature service the best properties were obtained with an alloy containing 12–15% chromium, 5–6% molybdenum, and 5·5–7% aluminium.[149] This alloy has a tensile strength of 62·5 tons/in.^{2}, and a 1000-hr. rupture strength of 14 tons/in.^{2} at 815° C.

Zinc alloys.—Wrought zinc–aluminium alloys containing 10–50% aluminium, which are heat-treated at 360° C. for 30 min. then quenched and aged, show very great ductility, having an elongation of 130% and reduction in area of almost 100% in a tensile test.[150] Small additions of copper and tin improved the ductility. It is suggested that the alloys are suitable for use as packing materials for hydraulic equipment.

Zirconium.—The melting, casting, working, and mechanical properties of zirconium have been described.[151]

Melting and casting

The casting fluidity of a number of pure metals and lead–tin and aluminium–silicon alloys has been investigated by Kondic and Koslowski[152]

using a modified spiral mould apparatus. They suggest that the fluidity of pure metals depends in particular on the viscosity and the heat content of the liquid metal. The interpretation of the results of experiments on alloys is more difficult, but similar factors to those applying to pure metals must be of importance. It is considered that the mechanical interference of growing dendrites on the flow have only a minor influence on the results of fluidity tests. The mode of solidification of cast billets has been reviewed by Scheuer[153] with particular reference to continuous casting processes. The heat transfer and temperature distribution in metal[154] and sand[155] moulds have been investigated. In the latter investigation it was found possible to treat the problem mathematically, to assign 'chilling powers' to various dry mould materials, and so to calculate approximately the freezing times of castings of simple shape in moulds of these substances. An analogous problem is that of deciding the optimum size and shape of risers in castings so as to provide a continuous feeding of the casting with metal until solidification is complete; the mathematical treatment of this problem has been considered.[156,157] High speed ciné-photography has been used to study the flow of metal into sand moulds.[158] Various types of gating system were used but none was found to prevent turbulence completely. In multiple ingate systems the ingates furthest from the runner had the fastest delivery; this could be balanced by reducing the total cross-sectional area of the ingates relative to the cross-sectional area of the runner. The absorption of gases by molten metal and their subsequent evolution when the metal solidifies have always been important problems for the foundry metallurgist. A good review of this topic, although mainly concerned with the physical chemistry of the process, has been given by Lepp.[159]

Aluminium.—The more specific problem of gas in aluminium and its alloys has been reviewed.[160] Two reviews on the die-casting process have appeared.[161,162] The grain-refinement of pure aluminium by small additions of a number of elements has been studied; the most effective are titanium, zirconium, and vanadium.[163] Boron was found to be effective for grain-refining aluminium–copper alloys. It has been suggested that this refinement is due, at least in part, to the formation of finely divided carbides of the grain-refining elements, which can act as nuclei for the growth of the aluminium crystals from the melt.[164] The segregation which occurs when aluminium–copper alloys solidify unidirectionally has been studied by Adams,[165] who considers that the main features of the segregation are due to intercrystalline flow of residual liquid to compensate for solidification shrinkage.

Copper.—A symposium on metallurgical aspects of non-ferrous melting and casting of ingots for working, organized by the Institute of Metals, was held in London in March, 1949. The majority of the papers were concerned with copper–base alloys. A general review of melting and casting methods was given by Bailey and Baker,[166] who discussed the mode of solidification, gas pick-up and removal, casting methods, and ingot structure. Waddington[167] described the procedure used in a modern works for the casting of tough-pitch copper, and Bradbury and Turner[168] described works practice in the casting of nickel silver (copper–nickel–zinc) alloys. Papers were given on the melting and casting of

aluminium–bronze,[169] and brasses.[170] Bond-Williams describes the melting and casting of phosphor bronze, discussing an improved melting and casting procedure, and a flux degassing process.[171] The pressure tightness of lead-free gunmetal sand castings (8—10% tin, 4—2% zinc) is improved by the presence of residual phosphorus (0·04–0·08%) in the metal after deoxidation.[172]

Magnesium.—Siebel[173] has discussed a number of improvements in magnesium technology. These include: a new alloy with 8·5% aluminium, 8% cadmium, 3% silver and 0·3% manganese which has a tensile strength of 50 kg./mm.^{2}, a yield strength of 41 kg./mm.^{2}, and an elongation of 5% ; the grain-refinement of magnesium alloys containing zinc by means of zirconium or cerium ; the grain-refinement of aluminium-bearing alloys by repeated melting and solidification *in vacuo* or by treatment with ferric chloride. Non-metallic inclusions in magnesium alloys may give rise to serious corrosion ; the nature of such inclusions and their prevention has been considered by Emley.[174] He shows that the inclusions in the final product do not arise from particles suspended in the melt before pouring, but arise, at the time of casting, from a number of causes. An important method for reducing the amount of such inclusions consists in the use of a viscous flux as a cover on the molten metal, the flux having suitable physical properties to enable a clean stream of metal to be poured. Magnesium alloys containing zirconium are an exception. The zirconium is most easily introduced into the metal by an alkali metal chlorozirconate, and this gives rise to particles in the melt which consist of chloride products of the alloying reaction entrapped in clusters of insoluble zirconium-rich particles. These particles cannot be removed by fluxing, settling, or filtration through metal gauze, and Emley suggests that zirconium-bearing alloys made by this method are inherently unreliable.

Corrosion and protection

The mechanism of the formation of films on metal surfaces has been reviewed by U. R. Evans.[175] Wagner[176] has discussed the process of growth of dry oxide and sulphide films on metals, and Valensi[177] has considered the more complex mechanism of the growth of double layer films on metals with two oxides. The mode and rate of formation of oxide films on alloys intended for high-temperature service is, of course, vital to their use, and a number of investigations on this subject have been reported. The oxidation rates of pure nickel,[178] and of nickel and nickel–chromium alloys[179] containing small amounts of other elements in solid solution have been investigated ; the added elements increase the rate of oxidation of nickel, but decrease that of chromium–nickel alloys. This decrease is considered to be due to the increase in the rate of diffusion of chromium atoms caused by the presence of the third element ; this results in a more rapid growth of a protective surface layer of chromium oxide. The oxidation of manganese in air in the temperature range 400–1100° C. follows a parabolic law ; the oxide layer consists wholly of Mn_3O_4 at temperatures up to 900° C. ; from 900–1100° C. increasing amounts of MnO are present in the film.[180] High-melting-point alloys

containing molybdenum sometimes show very rapid oxidation at high temperatures. Work on alloys of this type, mainly on an alloy containing 16% chromium, 25% nickel, 6% molybdenum, and the remainder iron, suggests that the rapid oxidation is due to the presence of gaseous molybdic oxide which catalyses the oxidation of iron; this is in agreement with the fact that an increased flow of air over the surface of the hot metal greatly reduces the rate of oxidation by sweeping away the gaseous molybdic oxide. The high temperature oxidation of a number of alloys of the metals chromium, tungsten, molybdenum, tantalum, niobium and nickel has been investigated.[182] Alloys in the systems chromium–tungsten, chromium–molybdenum, chromium–niobium–tungsten and chromium–tantalum–tungsten show oxidation rates which increase with decreasing chromium content. Chromium–tantalum alloys with 60–70% tantalum, chromium–niobium alloys with 40–50% niobium, and nickel–niobium alloys with 5–13% niobium have greater oxidation resistance than pure chromium. Chromium–tantalum–nickel alloys in the range 10–40% tantalum, 50–80% nickel, and 10–25% chromium have good oxidation resistance which is doubled by the addition of 1% calcium. Present tendencies in corrosion research have been reviewed by Lacombe,[183] who gives special attention to wet corrosion.

When the results of stress-corrosion tests on a wide range of materials were plotted as stress (5–50 kg./mm.^{2}) against life (in hours) on a log–log scale, a straight line relationship was obtained.[184]

Stress-corrosion tests on a number of high strength aluminium alloys have been described[185]; the addition of 0·07–0·21% vanadium and 0·07–0·65% copper to an aluminium alloy containing 4·5% zinc and 3·5% magnesium very greatly increases resistance to stress-corrosion.[186]

The relationship between stress-corrosion cracking and composition for a number of binary copper–base alloys has been investigated.[187] It is suggested that the solute element is more concentrated at the grain boundaries which become anodic to the body of the grains, accelerating local corrosion at the grain boundaries. Tensile stress accelerates the process by opening cracks and forming regions of high stress concentration at the end of each crack. The dezincification of brass by corrosive conditions has been reviewed by Colegate.[188]

A solution containing both selenious acid and sodium dichromate has been shown to give better protective coatings on magnesium alloys than solutions containing only one of these compounds.[189] A treatment which produces a protective coating of magnesium fluoride on magnesium alloys has been described[190]; it is claimed that this gives better protection than coatings produced by the dichromate process.

The corrosion of nickel in steam condensate has been shown to be due to the presence of carbon dioxide and air in a critical ratio in the steam supply; iron corrosion products increased the range of carbon dioxide concentration in which appreciable corrosion of nickel took place.[191]

The rate of corrosion of zinc in a mildly industrial atmosphere has been shown to depend on the weather conditions at the beginning of exposure.[192] If these were such as to cause a high rate of corrosion during the first five days of exposure, then the corrosion rate at the end of a year was still

greater than that of a specimen exposed under initial conditions which give a low rate.

The corrosion of a number of metals by motor fuels has been investigated.[193] Acid in alcohol fuels promotes corrosion ; water in other fuels may cause considerable corrosion since, under certain conditions, water droplets may settle on the metal surface and set up local cells.

References

[1] FIAT Reviews of German Science, 1939–46, notably the volumes on General Metallurgy (I and II) and Physics of Solids (I and II)
[2] 'Progress in Metal Physics I' (London, 1949)
[3] Prager, W., *J. appl. Phys.*, 1948, **19**, 540 ; *J. appl. Mech.*, 1948, **15**, 226
[4] Epstein, B., *J. appl. Phys.*, 1948, **19**, 140
[5] Hill, R., *Proc. roy. Soc.*, 1948 [A], **193**, 281 ; 1949 [A], **198**, 428
[6] Leschen, J. G., Carreker, R. P. and Holloman, J. H., Amer. Inst. min. metall. Engrs. Tech. Publication No. 2476, 1948 ; *Metal Technol.*, 1948, **15** (6)
[7] Carreker, R. P., Leschen, J. G. and Lubahn, J. D., ibid., Tech. Publ. No. 2477 ; *Metal Technol.*, 1948, **15** (6)
[8] Fredrickson, J. W. and Eyring, H., ibid., Tech. Publ. No. 2423 ; *Metal Technol.*, 1948, **15** (5)
[9] McCance (Sir) A., *J. Iron Steel Inst.*, 1949, **163**, 241
[10] Nabarro, F. R. N., *Metallurgia, Manchr.*, 1949, **40**, 199 ; *Z. Metallk.*, 1949, **40**, 81
[11] Mott, N. F., *Physica*, 1949, **15**, 119 ; *Research*, 1949, **2**, 162
[12] Dean, W. R. and Mann, E. H., *Proc. Camb. phil. Soc.*, 1949, **45**, 131
[13] Bragg (Sir) L., ibid., 125
[14] Eshelby, J. D., *Phil. Mag.*, 1949, **40**, 903
[15] Cottrell, A. H. and Jaswon, M. A., *Proc. roy. Soc.*, 1949 [A], **199**, 104
[16] Bragg (Sir) L., *Physica*, 1949, **15**, 83
[17] Bragg (Sir) L. and Lomer, W. M., *Proc. roy. Soc.*, 1949 [A], **196**, 171
[18] Lomer, W. M., ibid., 182
[19] Heidenreich, R. D., *J. appl. Phys.*, 1948, **19**, 1190
[20] Brown, A. F., *Nature*, 1949, **163**, 961
[21] Gwathmey, A. T., Pittsburgh International Conference on Surface Reactions (Proceedings), 1948, 66
[22] Holden, A. N., Amer. Soc. Metals Preprint No. 35, 1949
[23] Tiedema, T. J., *Acta crystall.*, 1949, **2**, 261
[24] Cottrell, A. H. and Gibbons, D. F., *Nature*, 1948, **162**, 488
[25] Andrade, E. N. da C. and Randall, R. F. Y., *Nature*, 1948, **162**, 890
[26] Holden, A. N. and Hollomon, J. H., *J. Metals*, 1949, **1**, 179
[27] Schwartzbart, H. and Low, J. R., ibid., 637
[28] Cahn, R. W., *J. Inst. Met.*, 1949, **76**, 121
[29] Guinier, A. and Lacombe, P., *Métaux et Corrosion*, 1948, **23**, 212
[30] Eshelby, J. D., *Proc. roy. Soc.*, 1949 [A], **197**, 396
[31] Potter, E. V., U.S. Bur. Mines Rep. Invest., No. 4194, 1948
[32] Boulanger, C., *Rev. Métall.*, 1949, **46**, 255
[33] Smoluchowski, R. and Wu, T. L., *Phys. Rev.*, 1949, **75**, 345
[34] T'ing-Sui Kê, ibid., **76**, 579
[35] Bozorth, R. M., Mason, W. P., McSkimin, H. J. and Walker, J. G., ibid., **75**, 1964
[36] Reinacher, G. and Scheil, E., *Z. Metallk.*, 1948, **39**, 231
[37] Zener, C., *Physica*, 1949, **15**, 111
[38] Koehler, J. S., *Phys. Rev.*, 1949, **75**, 1626
[39] T'ing-Sui Kê, ibid., 1948, **74**, 914
[40] Dijkstra, L. J., *J. Metals*, 1949, **1**, 252
[41] Smith, C. L., *Proc. phys. Soc., Lond.*, 1948, **61**, 201
[42] Wood, W. A. and Rachinger, W. A., *J. Inst. Met.*, 1949, **75**, 571 ; ibid., **76**, 237 ; Wood, W. A. and Wilms, G. R., ibid., **75**, 693
[43] Lacombe, P. and Beaujard, L., *Rev. Métall.*, 1948, **45**, 317
[44] Lacombe, P. and Berghézan, A., *Physica*, 1949, **15**, 161
[45] Crussard, Ch. and Guinier, A., *Rev. Métall.*, 1949, **46**, 61

[46] Tiedema, T. J., May, W. and Burgers, W. G., *Nature*, 1948, **162**, 740; *Acta crystall.*, 1949, **2**, 151
[47] Lacombe, P. and Berghézan, A., *C.R. Acad. Sci., Paris*, 1949, **228**, 93
[48] Beck, P. A. and Sperry, P. R., *J. Metals*, 1949, **1**, 240
[49] Burgers, W. G., *Physica*, 1949, **15**, 92
[50] Beck, P. A., *J. appl., Phys.*, 1948, **19**, 507
[51] Beck, P. A. and Hsun Hu, *J. Metals*, 1949, **1**, 627
[52] Cohear, P. and Lejeune, J. M., *Rev. Métall.*, 1949, **46**, 439
[53] Kronberg, M. L. and Wilson, F. H., *J. Metals*, 1949, **1**, 501
[54] Hofmann, W. and Trautmann, B., *Z. Metallk.*, 1948, **39**, 293
[55] Thall, B. M. and Newcombe, J. A., *Trans. Canad. Inst. Min. Met.*, 1948, **51**, 223
[56] Smigelskas, A. and Barrett, C. S., *J. Metals*, 1949, **1**, 145
[57] Turnbull, D., *Phys. Rev.*, 1949, **76**, 471
[58] Achter, M. R. and Smoluchowski, R., ibid., 470
[59] Seitz, F., ibid., 1948, **74**, 1513
[60] Bragg (Sir) L., *Advancement of Science*, 1948, **5**, 165; *Science*, 1948, **108**, 455
[61] Pauling, L., *Proc. roy. Soc.*, 1949 [A], **196**, 343; *Nature*, 1948, **161**, 1019; *Physica*, 1949, **15**, 23; Pauling, L. and Ewing, F. J., *Rev. mod. Physics*, 1948, **20**, 112
[62] Hume-Rothery, W., *Physica*, 1949, **15**, 29
[63] Idem, *Proc. roy. Soc.*, 1949 [A], **197**, 17
[64] Raynor, G. V. and Waldron, M. B., ibid., 1948 [A], **194**, 362
[65] Douglas, A. M. B., *Nature*, 1948, **162**, 565
[66] Raynor, G. V. and Waldron, M. B., *Phil Mag.*, 1949, **40**, 198
[67] Pfeil, P. C. L. and Raynor, G. V., *Proc. roy. Soc.*, 1949 [A], **197**, 320
[68] Raynor, G. V. and Frost, B. R. T., *J. Inst. Met.*, 1949, **75**, 777
[69] Raynor, G. V. and Smith, R. A., ibid., **76**, 389
[70] Raynor, G. V. and Hume-Rothery, W., *Trans. Faraday Soc.*, 1948, **44**, 29
[71] Raynor, G. V. and Wakeman, D. W., *Phil. Mag.*, 1949, **40**, 404
[72] Ellwood, E. C., *Nature*, 1949, **163**, 772
[73] Schubert, K., *Metallforsch.*, 1947, **2**, 349
[74] Hume-Rothery, W. and Boultbee, T. H., *Phil. Mag.*, 1949, **40**, 71
[75] Schwab, G. M. and Petrousos, G., *Research*, 1948, **1**, 717
[76] Brommelle, N. S. and Phillips, H. W. L., *J. Inst. Met.*, 1949, **75**, 529
[77] Sully, A. H., Hardy, H. K. and Heal, T. J., ibid., **76**, 269
[78] Köster, W., *Z. Metallk.*, 1948, **39**, 211
[79] Schrader, A., *Metall*, 1949, **3**, 111
[80] Köster, W., *Z. Metallk.*, 1948, **39**, 352
[81] Köster, W., Zwicker, U. and Moeller, K., ibid., 225
[82] Paul, J. M. and Beard, G. V., *J. Phys. colloid Chem.*, 1948, **52**, 750
[83] Köster, W. and Rauscher, W., *Z. Metallk.*, 1948, **39**, 178
[84] Potter, E. V. and Huber, R. W., *Trans. Amer. Soc. Metals*, 1949, **41**, 1001
[85] Carlile, S. J., Christian, J. W. and Hume-Rothery, W., *J. Inst. Met.*, 1949, **76**, 169
[86] Jaffee, R. I. and Nielsen, H. P., Amer. Inst. min. metall. Engrs., Tech. Publ. No. 2420; *Metal Technol.*, 1948, **15**, 5.
[87] Horn, L. and Bassermann, C., *Z. Metallk.*, 1948, **39**, 272
[88] Perretti, E. A. and Carapella, S. C., *Trans. Amer. Soc. Metals*, 1949, **41**, 947
[89] Teitel, R. J. and Cohen, M., *J. Metals*, 1949, **1**, 285
[90] Chatterjee, G. P. and Sidhu, S. S., *Phys. Rev.*, 1949, **76**, 175
[91] Bystrom, A. and Almin, K. E., *Acta chem. Scand.*, 1948, **1**, 76
[92] McMullin, J. G. and Norton, J. T., *J. Metals*, 1949, **1**, 46
[93] Raynor, G. V., *Trans. Faraday Soc.*, 1948, **44**, 15
[94] Jollivet, L., *C.R. Acad. Sci., Paris*, 1949, **228**, 1128
[95] Idem, ibid., 1495
[96] Nial, O., *Svensk kem. Tidskr.*, 1947, **59**, 172
[97] Vogel, R. and Gilde, W., *Z. Metallk.*, 1949, **40**, 121
[98] Long, J. R., Hayes, E. T., Root, D. C. and Armantrout, C. E., U.S. Bur. Mines Rep. Invest., No. 4463, 1949
[99] Heumann, T., *Z. Metallk.*, 1948, **39**, 45
[100] Henglein, E. and Köster, W., ibid., 391
[101] Gebhardt, E., ibid., 1949, **40**, 136
[102] Raub, E. and Engel, M., ibid., 1948, **39**, 172
[103] Nowotny, H. and Kieffer, R., *Metallforsch.*, 1947, **2**, 257

[104] Norton, J. T. and Mowry, A. L., *J. Metals*, 1949, **1**, 133
[105] Sindeband, S. J., ibid., 198
[106] Coles, B. R., Hume-Rothery, W. and Myers, H. P., *Proc. roy. Soc.*, 1949 [A], **196**, 125
[107] Epremian, E. and Harker, D., *J. Metals*, 1949, **1**, 267
[108] Henglein, E. and Kohsok, H., *Rev. Métall.*, 1949, **45**, 569
[109] Wilson, A. S. and Rundle, R. E., *Acta crystall.*, 1949, **2**, 126
[110] Rundle, R. E. and Wilson, A. S., U.S. Atomic Energy Commission Publication, 1948, AECD/2388 ; *Acta crystall.*, 1949, **2**, 148
[111] Bacon, G. E. and Thewlis, J., *Proc. roy. Soc.*, 1949 [A], **196**, 50
[112] Sidhu, S. S., *J. appl. Phys.*, 1948, **19**, 639
[113] Seigel, S. and Shull, C. G., *Phys. Rev.*, 1948, **74**, 1255 ; 1949, **75**, 1008
[114] Borelius, G., *Physica*, 1949, **15**, 135
[115] Raub, E., *Z. Metallk.*, 1949, **40**, 46
[116] Newkirk, J. B. and Smoluchowski, R., *Phys. Rev.*, 1949, **76**, 471
[117] Betteridge, W., *J. Inst. Met.*, 1949, **75**, 559
[118] Borelius, G. and Larsson, L. E., *Ark. Mat. Ast. Fys.*, 1948, **35A**
[119] Hardy, H. K., *J. Inst. Met.*, 1949, **75**, 559
[120] Smoluchowski, R., *Phys. Rev.*, 1948, **74**, 343 ; *Physica*, 1949, **15**, 179
[121] Guinier, A., *Physica*, 1949, **15**, 148
[122] Geisler, A. H., Amer. Inst. min. metall. Engrs. Tech. Publ. No. 2436, 1948 ; *Metal Technol.*, 1948, **15**
[123] Geisler, A. H. and Hill, J. K., *Acta crystall.*, 1948, **1**, 238
[124] Castaing, R., *C.R. Acad. Sci., Paris*, 1949, **228**, 1341
[125] Finlay, W. L. and Hibbard, W. R., Amer. Inst. Min. metall. Engrs. Tech. Publication No. 2470, 1948 ; *Metal Technol.*, 1948, **15**
[126] Geisler, A. H. and Newkirk, J. B., ibid., Tech. Publ. No. 2444, 1948
[127] Grant, N. J. and Lane, J. R., *Trans. Amer. Soc. Metals*, 1949, **41**, 95
[128] Harrington, R. H., ibid., 443
[129] Vosskühler, H., *Metall*, 1948, 251
[130] Zambrow, J. L. and Fontana, M. G., *Trans. Amer. Soc. Metals.*, 1949, **41**, 480
[131] Chadwick, R. and Hooper, W. H. L., *J. Inst. Met.*, 1949, **75**, 609
[132] Chadwick, R., Richards, T. Ll. and Sumner, K. G., ibid., 627
[133] Lemon, R. C. and Hunsicker, H.Y., Amer. Soc. Metals Preprint No. 34, 1949
[134] Betteridge, W., Wilson, C., Haughton, M. A. and Morgan, W., *J. Inst. Met.*, 1949, **75**, 641
[135] Crowther, J., ibid., **76**, 201
[136] Cook, M., Fourth Empire Min. Met. Congr. Paper No. H–1 **12**, 1949
[137] Schwope, A. D., Smith, K. F. and Jackson, L. R., *J. Metals*, 1949, **1**, 409
[138] Anderson, A. R., Swan, E. F. and Palmer, E. W., *Proc. Amer. Soc. Test. Mater.*, 1946, **46**, 678
[139] Gohn, G. R. and Arnold, S. M., ibid., 741
[140] Hodge, W., Jaffee, R. I., Dunleavy, J. G. and Ogden, H. R., Amer. Inst. min. metall. Engrs. Tech. Publ. No. 2422, 1948 ; *Metal Technol.*, 1948, **15**, (5)
[141] Samuels, L. E., *J. Inst. Met.*, 1949, **76**, 91
[142] Baker, W. A. and Hallowes, A. P. C., ibid., **75**, 741
[143] Cornet, I., Amer. Inst. min. metall. Engrs. Tech. Publ. No. 2419, 1948 ; *Metal Technol.*, 1948, **15**, (5)
[144] Jackson, J. H., Frost, P. D., Loonam, A. C., Eastwood, L. W. and Lorig, C. H., *J. Metals*, 1949, **1**, 149
[145] Mellor, G. A. and Ridley, R. W., *J. Inst. Met.*, 1949, **75**, 679
[146] Gohn, G. R. and Ellis, W. C., *Proc. Amer. Soc. Test. Mater.*, 1948, **48**, 801 ; Phelps, H. S., Kahn, F. and Magee, W. P., ibid., 815
[147] Greenwood, J. N. and Cole, J. H., *Metallurgia, Manchr.*, 1949. **39**, 121
[148] Idem, ibid., 241
[149] Guy, A. G., *Trans. Amer. Soc. Metals*, 1949, **41**, 125
[150] Sauerwald, F., *Arch. Metallk.*, 1949, **3**, 165
[151] Hayes, E. T., Dilling, E. D. and Roberson, A. H., Amer. Soc. Metals Preprint No. 32, 1949
[152] Kondic, V. and Kozlowski, H. J., *J. Inst. Met.*, 1949, **75**, 665
[153] Scheuer, E., ibid., **76**, 103
[154] Udy, M. C. and McIntire, H. O., *Trans. Amer. Foundrym. Ass.*, 1947, **55**, 208

[155] Ruddle, R. W. and Mincher, A. L., *J. Inst. Met.*, 1949, **76**, 43
[156] Faber, A. F. and Doll, D. T., *Trans. Amer. Foundrym. Ass.*, 1947, **55**, 461
[157] Caine, J. B., *Trans. Amer. Foundrym. Soc.*, 1948, **56**, 492 ; *Amer. Foundryman*, 1949, **15**, 46
[158] Johnson, W. H. and Baker, W. O., *Trans. Amer. Foundrym. Soc.*, 1948, **56**, 389 ; *Foundry, Lond.*, 1948, **76**, 68
[159] Lepp, H., *Vide*, 1948, **3**, 433
[160] Castro, R. and Armand, M., *Rev. Métall.*, 1949, **45**, 594
[161] Duport, J., *Fonderie*, 1948, **35**, 1371
[162] Halliday, W. M., *Metal Ind., Lond.*, 1949, **74**, 3
[163] Eborall, M. D., *J. Inst. Met.*, 1949, **76**, 295
[164] Cibula, A., ibid., 321
[165] Adams, D. E., ibid., **75**, 809
[166] Bailey, G. L. and Baker, W. A., ibid., 285
[167] Waddington, R. H., ibid., 311
[168] Bradbury, E. J. and Turner, P. G., ibid., 373
[169] Murphy, A. J. and Callis, G. T., ibid., 325
[170] Cook, M. and Fletcher, N. F., ibid., 353
[171] Bond-Williams, N. I., ibid., 339
[172] Glaisher, W. H., **76**, 377
[173] Siebel, G., *Z. Metallk.*, 1948, **39**, 97 ; *Metall*, 1948, 357
[174] Emley, E. F., *J. Inst. Met.*, 1949, **75**, 431, 481
[175] Evans, U. R., Pittsburgh International Conference on Surface Reactions (Proceedings), 1948, 71
[176] Wagner, C., ibid., 77
[177] Valensi, G., *Rev. Métall.*, 1948, **45**, 205
[178] Kubaschewski, O. and Golbeck, O. v., *Z. Metallk.*, 1948, **39**, 158
[179] Horn, L., ibid., 1949, **40**, 73
[180] Gumick, R. S. and Baldwin, W. M., Amer. Soc. Metals Preprint No. 9, 1949
[181] Leslie, W. C. and Fontana, M. G., *Trans. Amer. Soc. Metals*, 1949, **41**, 1213
[182] Kubaschewski, O. and Schneider, A., *J. Inst. Met.*, 1949, **75**, 403 ; Kubaschewski, O. and Spiedel, H., ibid., 417
[183] Lacombe, P., *Rev. Métall.*, 1948, **45**, 2
[184] Wassermann, G., *Z. Metallk.*, 1948, **39**, 66
[185] Logan, H. L. and Hessing, H., *J. Res. nat. Bur. Stand.*, 1948, **41**, 69
[186] Bungardt, W., *Z. Metallk.*, 1948, **39**, 247
[187] Thompson, D. H. and Tracy, A. W., *J. Metals*, 1949, **1**, 100
[188] Colegate, G. T., *Metal Ind., Lond.*, 1948, **73**, 483
[189] Whitby, L., *Metallurgia, Manchr.*, 1949, **39**, 233
[190] Staesche, M., *Arch. Metallk.*, 1948, **2**, 99
[191] Wesley, W. A. and Copson, H. R., *J. electrochem. Soc.*, 1949, **95**, 226
[192] Ellis, O. B., Amer. Soc. Test. Mat. Preprint No. 10, 1949
[193] Schläpfer, P. and Bukowiecki, A., *Schweiz. Arch. Angew. Wiss. Techn.*, 1948, **14**, 257; *Métaux, Corrosion*, 1948, **23**, 267

EXTRACTION AND REFINING (EXCLUDING ELECTROMETALLURGY) (S. W. Smith, C.B.E., D.Sc., A.R.S.M.)

THE year under review has been notable in regard to valuable contributions made by British metallurgists to records of progress in the widely differing fields of technology by which the increasing demands for non-ferrous metals are being met. The references give some of the more important sources from which information may be gathered in closer detail of specific matters which it would be impossible to cover by a short review. Attention may, however, be directed to one or two of the events during the past year which have led to important contributions from competent authorities.

Foremost in these events has been the meeting in congress,[1] after a lapse of nearly 20 years, of the representatives of the various bodies constituting the Empire Council of Mining and Metallurgical Institutions. This Congress, which met in July, attracted large numbers of overseas visitors to the meetings and discussions which took place in London and in Oxford. Brief references will be made later to the papers presented at those sessions at which matters were discussed of immediate concern to those whose province it is to ensure the supply of non-ferrous metals, upon which the vast metallurgical industries of the world are so largely dependent.

Timed to coincide with this Congress, was an important Symposium of eight Sessions on the Refining of Non-Ferrous Metals arranged under the auspices of the Institution of Mining and Metallurgy,[2] and at which some 19 papers were presented and discussed.

Brief reference was made last year to the Symposium arranged by the Faraday Society[3] on the Physical Chemistry of Extraction Metallurgy—more particularly in relation to reduction processes. The papers presented and discussed became available in their final form at a later date and some indication will be given of their scope.

Progress in regard to the search for new sources of supply of the non-ferrous metals, to the concentration of low-grade material by flotation and other dressing operations, and to the more efficient extraction and refining of the various metals—both in major and minor tonnages—is manifested by the contributions made to the professional bodies in this country and overseas and published in their Transactions.

The papers presented at a Belgian congress[4] in 1947 became available in 1949. These cover many aspects of extraction and refining.

The position in France[5] (and in the French colonies), with regard to the smelting of non-ferrous metals was reviewed by R. S. Lajeunesse. Official Reports[6,7,8] were published by H.M. Stationery Office on the work of various committees dealing with non-ferrous metals and minerals.

The physico-chemical principles of extraction metallurgy

The papers presented and discussed at the Faraday Society's Symposium in 1948[3] are now available. The paper by C. F. Goodeve dealt at some length with the kinetics and thermodynamics of extraction metallurgy and with the relationships between the gaseous, liquid and solid states of the reactions involved—particularly the ionic constitution of these phases. The problems presented by refining are discussed in relation to the high mutual solubility of metals and their compounds in the liquid state. Roasting and reduction processes are surveyed by C. W. Dannatt and H. J. T. Ellingham. Oxidation and reduction processes are discussed from the point of view of the free energy data of the formation of many metallic oxides and sulphides. It is shown that thermodynamic data give indications of what might be achieved in separating undesired elements and also in affording a guide as to what may prove to be beyond the possibility of achievement.

Other papers by B. A. Rose, G. J. Davis and H. J. T. Ellingham, by J. S. Anderson, by A. Juliard, R. Rayet and A. Ludé, by L. M. Pidgeon and J. A. King, by P. Gross, C. S. Campbell, P. J. C. Kent and D. L. Levi,

and by P. Gross and M. Warrington, covered such questions as the dissociation of carbon monoxide during the reduction of metallic oxides, the vapour pressure of magnesium in the ferro-silicon reduction of that metal, equilibria data of aluminium monohalides, and the reduction of zinc sulphide by iron under reduced pressure.

Mineral dressing

The present-day trends in mineral dressing were discussed at a Session of the Empire Congress[1] at which four important papers were presented by representatives of this branch of metallurgical activity in Canada, in Southern Africa, and in Australia.

Close attention is being given to the problems which arise in recovering finely disseminated mineral particles from ore bodies of low grade which can only be made economic by operating on large tonnages. The dressing of non-sulphide minerals continues to make satisfactory progress. Of the methods employed, the older one of gravity separation still has important applications, although, of course, enormous tonnages of material are now being subjected to fine grinding for the purposes of selective flotation. It is in the field of suitable activators and depressants that notable progress is being made, covering a wide range of mineral species.

Even the optimum conditions for the successful recovery of *similar* species may vary considerably according to the proportions in which they are present in the ore-bodies under treatment. For instance, the low-grade copper deposits of Arizona (yielding about 1% of copper) and the deposits of relatively high grade in Northern Rhodesia (yielding from 3 to 4%) present problems peculiar to themselves.

Other problems, such as the flotation of cassiterite, are receiving close attention by those who are throwing fresh light on the physico-chemical aspects of mineral dressing. An interesting development in America has been the activation and flotation of quartz itself, using calcium ions as activators. The use of magnetic separators, so long employed in concentrating wolfram from tin ores, has received attention, while electrostatic separation has been successfully employed for rutile and zircon.

Future supplies of the non-ferrous metals

Although the activities during the past year have been largely directed towards the further exploitation of known metalliferous deposits, there has been intensive application of the newer methods of prospecting afforded by the rapid advances in the technique of geophysical prospecting. Gone are the days when, within living memory, the discovery of new sources of supplies depended very largely on the individual prospector.

While the newer methods belong, perhaps, to the realm of applied physics rather than to that of applied chemistry, nevertheless, the results of such work are of profound interest and importance to the producer of non-ferrous metals who realizes only too vividly that the present sources are, at the best, but 'wasting assets.'

Nine of the papers presented at the Empire Congress[1] dealt in some detail with the known resources in Australia, South Africa, Canada, Malaya, British West Africa, the East African Colonies, India, Southern

Rhodesia, Northern Rhodesia and other Empire territories. Three other papers were devoted more specifically to modern methods of prospecting for minerals. Geological mapping, which is now aided by aerial photography, is followed by geophysical exploration in promising areas and finally by the crucial, though costly, procedure of diamond-drilling and the recovery of the cores for analytical scrutiny. The literature of the year shows that intensive activity is proceeding on these lines in almost every country in the world. Some prominence is given to the further search for uranium minerals.

Brief reviews will now be given of the contributions which have appeared in regard to those non-ferrous metals which, from the point of view of gross tonnages, are of outstanding importance.

These will be followed by some notes of the recorded developments in the production of those metals which are classified either as the precious metals or as the less common and rarer metals.

Copper

Modern North American practice in copper pyrometallurgy was reviewed by W. B. Boggs,[9] formerly Smelter Superintendent at the Noranda Mines (Quebec).

The smelting of flotation concentrates in reverberatory furnaces has, of course, been the general practice now for many years but the advances in construction and in working efficiency have been striking. The larger furnaces of today have hearths of 100 ft. by 33 ft., no fire-boxes, tamped magnesite bottoms, magnesite-brick side-walls, suspended magnesite-brick roofs and are fired with fuel oil or pulverized coal and in some cases with natural gas. Some 2000 tons of solid material are smelted per day with a fuel ratio of 10 tons of ore to 1 ton of coal. At Noranda, a furnace of this type was in continuous operation for over six years, repairs being effected by hot-patching from the outside without interfering with production. A decision as to whether the concentrates shall be roasted and the hot calcine then charged into the furnace, or whether they can be charged direct from the concentrators and still retaining some 10% moisture, depends upon the character of the mined ore as regards sulpihde minerals. The latter procedure can be followed in the cases of concentrates from the so-called 'porphyries' of Arizona and the Northern Rhodesian deposits which are relatively low in pyritic sulphides. The 'porphyries' although containing only from 0·8–2·0% Cu can be concentrated up to 25–40% Cu and the Rhodesian ores of 3–4% Cu up to 55% Cu.

The primary sulphides of the Cambrian Shield in Canada, however, carry a larger percentage of pyrite and pyrrhotite and so yield a lower ratio of concentration and therefore need roasting to lower the sulphur content and to give a sufficiently high grade of matte.

Other matters upon which the success of large-scale smelting depends are discussed at some length, e.g. Cottrell precipitation, multiclones, suitable refractories, converters and holding furnaces.

The fire refining of copper in reverberatory and in rotary furnaces was reviewed by H. J. Miller[10] and recent trends were discussed. One of the

outstanding developments in recent years has been the production of high-conductivity copper from certain high-purity blister coppers, following the procedure by which Lake copper was formerly marketed in the U.S.A. To satisfy the requirements of the electrical industries, however, the process is limited to the relatively few blister coppers in which the precious metal contents are negligible and in which elements such as Bi, Se, and Te are only present in traces. Otherwise, electrolytic refining becomes essential.

The trends in refining and casting of high-conductivity and of oxygen-free copper at the Mufulira and Roan Antelope Mines of Northern Rhodesia were discussed by R. H. Bauld.[11] The possibilities and difficulties of continuous casting were also considered.

A paper on the electrolytic refinery at Nkana[12] was also presented by the staff of that establishment but this aspect of refining is beyond the scope and intention of the present review.

R. C. Trumbull, W. Hardick and E. G. Lawford[13] reviewed at some length the treatment, by a modification of the Henderson process, of pyrites cinders derived from cupriferous pyrites exported in past years to the U.S.A. from Rio Tinto, primarily for the production of sulphuric acid. The residues from the roasting operation contained, in addition to some 50–60% of iron, substantial amounts of copper, lead and zinc with some gold and silver. Proportions of these elements were profitably extracted before sintering the cinders for shipment to the iron works. Sections of the paper dealt with the chloridizing roast, the extraction of copper, gold and silver, the recovery of zinc and sodium sulphate and the extraction of lead.

H. R. Potts and E. G. Lawford[14] described the Orkla process for the recovery of sulphur from smelter gases as practised at Rio Tinto. This process was originally established in Norway by N. E. Lenander and was subsequently applied, first at San Domingos (Portugal) by Messrs. Mason and Barry and later at Rio Tinto. It is essentially a compromise in blast furnace practice whereby the pyritic smelting of copper ores to form a matte is accompanied by a recovery of sulphur from the issuing gases, the furnaces being specially fitted for this purpose with closed tops and bells.

The authors discuss the theory of the reactions from a quantitative analysis of the products and comment on the lines upon which a more efficient recovery of sulphur might be made, having regard to the inherent difficulties of attempting the oxidation of iron sulphide with efficient reduction of SO_2 in one and the same vessel and in contiguous zones within that vessel. The merits of the Orkla method, however, as practised at Rio Tinto, is that a yield of 3 tons of sulphur per ton of coke has been obtained, compared with 2 tons of sulphur per ton of coke by other processes. The presence of arsenic in the ores at Rio Tinto has prevented the use of catalysis which is a feature of the Norwegian practice. Arsenic affects the viscosity of sulphur and the temperature at which condensation begins.

An ingenious adjunct to the operations is the means taken to free the sulphur from arsenic whereby the percentage is reduced from 2% to a few parts per million. At the same time the ash is virtually eliminated.

Experiments on the removal of selenium and tellurium from blister and fire-refined copper were made by W. A. Baker and A. P. O. Hallowes[15] as alternatives to the removal by electrolytic copper refining in cases where there may be an economic incentive to do so. They have approached the problem, first, by aiming at the removal during the conversion of matte either by volatilization or by selective converting and secondly, by the addition of calcium and other elements during fire-refining.

Other papers are included in the References.[16,17,18]

Lead

An outstanding paper of interest to both metallurgical and chemical technologists was presented to the Empire Congress by W. S. Kirkpatrick,[19] in which he described in some detail a unique integration of metallurgical and chemical operations, which is made possible by the vast tonnages treated, at the plants of the Consolidated Mining and Smelting Co. of Canada at Trail, British Columbia.

This integration has for its object the economic utilization of waste gases which formerly polluted the neighbouring valleys and led to the setting up of a convention and tribunal between the United States and Canada, as the smelters are situated only seven miles from the international boundary.

Not only is the sulphur dioxide from the roasting furnaces for zinc concentrates and for lead concentrates used for the manufacture of sulphuric acid, but the acid so produced leads, in conjunction with synthetic ammonia and phosphate rock, to the production of ammonium sulphates, nitrates and phosphates. Oxygen from water electrolysis and low-temperature air fractionation is used for enriching the air in the zinc roasting operations; the poorer gases from the lead sintering plant are collected in ammonia, forming, in turn, sulphite, bisulphite and sulphate (by reaction with sulphuric acid); this releases sulphur dioxide as a rich gas which goes to enrich further the zinc roaster gases.

A favourable market situation for fertilizers has enabled the supply of sulphuric acid to be augmented by roasting iron sulphide tailings from the concentrators. Other useful products are obtained as the result of integration between the various processes which are shown diagrammatically by a flow-sheet.

Two papers by F. A. Green[20,21] deal with the lead-sintering practice at Port Pirie (South Australia) and with the refining of lead and associated metals at the same smelter, where the whole of the output of lead concentrates from the Broken Hill Mines are treated. Investigations have been made in the U.S.A. of the effect of high copper content in the charges for lead blast furnaces by A. G. Collins.[22] It is found that any advantages which may accrue from such high copper content are more than offset by increased costs of processing and by metal losses.

W. T. Isbell[23] gave a review of the metallurgy of lead.

Zinc and cadmium

In the field of zinc metallurgy considerable progress has been made in the development of equipment. Thus the American Metal Company at their Blackwell Works is building a sinter machine 168 ft. long and 12 ft.

wide. It is estimated the machine will treat 600 tons of sulphide concentrates per day.[23a]

The New Jersey Zinc Company is operating a flash roasting unit capable of treating 250 tons of flotation concentrates per day.[23a] Interest is being shown in a number of questions on the possible application of the 'fluo-solids' process to zinc blende roasting, but so far no commercial unit has been reported.

In the distillation section, progress has been made in the application of controlled humidity drying of retorts,[24] although at the moment the main application appears to be in the more rapid testing of experimental batches of retorts. The New Jersey Zinc Company (Pa.) announce the application to vertical retorts of a mechanically operated condenser in which the vapour is cooled by a shower of zinc raised on the condenser by means of a paddle agitator electrically driven. Cooling is provided by means of water-cooled coils immersed in the zinc bath.[25]

In cadmium metallurgy increasing attention is being paid to the recovery of minor impurities such as gallium, indium, thallium and germanium.[26] Bunker Hill announce a preliminary stage in the treatment of their cadmium-containing lead blast-furnace fume: this consists in fusing on a reverberatory furnace with silica additions; the cadmium is volatilized and recovered as a high-grade fume in a bag house.[27]

Methods of refining zinc and cadmium have been reviewed.[27a]

Tin

E. H. Jones[28] discussed the factors involved in a choice of procedure for the refining of tin. This choice is largely determined by the nature of the impurities with which the cassiterite is associated. These tend to accompany it and the earthy matter in the gravity concentrates and must be substantially removed at one stage or another. The tungsten mineral wolframite is of course separated magnetically or, more completely, by roasting and leaching. Flotation separates a number of unwanted minerals although some compromise is unavoidable when SnS is present. It has, however, now largely replaced calcination although in certain circumstances the latter is still retained, e.g. when the main impurities are sulphur and arsenic, or when it forms part of an acid-leaching technique.

Consideration was given to the part played by liquation in refining processes and to the equipment for separating skimmings and dross. Electrolytic, distillation, and other specialized processes were reviewed.

New tin-smelting projects[29] in the U.S.A. were reported together with further work on tin research.

H. L. Malan[30] contributed an account of the Ashcroft–Elmore process for the recovery of tin electrolytically from low-grade concentrates and complex ores.

A new and enlarged edition of the text-book 'Tin' by C. L. Mantell[31] is available. It covers a wide field and contains much up-to-date information.

Nickel

A comprehensive review of the past and present position of the nickel industry was given by Sir William Griffiths.[32] A new feature of the procedure at Copper Cliff is the progressive displacement of the Orford process

(which has been such an important and essential stage in the separation of nickel sulphides from those of copper during the past 60 years) by an alternative operation in which the nickel-rich matte (still containing copper) is subjected to controlled cooling. After crushing and flotation, followed by magnetic separation, the high-nickel fraction provides a nickel oxide sinter (low in copper and precious metals) which is suitable for refining, either by electrolysis or by the Mond carbonyl process. It can, moreover, be added direct to steel furnaces for the production of alloy steels.

Cobalt

The variety of uses to which this metal is now put has stimulated both demand and production. An admirable monograph by Roland S. Young,[34] with some 260 references, covers a very wide field and includes a summary of progress in the extraction and refining of the metal up to the date of publication. Descriptions are given of the operations in the Belgian Congo, in Northern Rhodesia and in French Morocco. Mention is also made of the part played for many years by the Deloro Smelting and Refining Co. of Ontario.

Due reference is given to the hydrometallurgy of cobalt leading up to electro-deposition.

P. S. Bryant[35] described in detail the operations of cobalt refining by the Murex Company at Rainham (Essex). He recorded the success with which carefully purified oxides can be reduced either to rondelles or to metal powder in the final stages of the treatment of shipments from overseas of the crude iron–cobalt–copper alloys.

H. L. Talbot and H. N. Hapker[36] described their investigations at Nkana (N. Rhodesia) on the leaching of cobalt concentrates and also of the matte resulting from the smelting of such concentrates, as alternatives to the present practice of slagging off cobalt in the converter stage and re-smelting to an iron–cobalt–copper alloy under reducing conditions in electric furnaces. The aim of their work has been to enable cobalt to be deposited by electrolysis from purified solutions of cobalt sulphate. The need for a change in procedure has arisen from a lowering in the cobalt content of the ores and of an increasing ratio of iron to cobalt, both factors making it more difficult to produce an exportable alloy which is acceptable to the refiners.

Investigations on the further selective concentration of cobalt minerals have not yet indicated any satisfactory method of separating the mineral carrolite from chalcopyrite and pyrite, either by flotation or by gravity methods. It was this difficulty which prompted their investigations.

H. R. Wells[37] and others have recorded work on the concentration of copper–cobalt ores in Idaho.

Antimony

The occurrence of antimony in association with gold at the Murchison Goldfields (Transvaal)[38] has led to a procedure by which a proportion of the antimony present in the ore is recovered as a concentrate containing 60–75% antimony. Objectionable impurities, such as nickel, copper,

arsenic, and lead minerals, are largely removed during the concentration of the gold by blanket strakes, jigs and by flotation. The resulting pulp is conditioned for the flotation of the antimony mineral, which, after gravity treatment to remove the remaining gold and arsenic, is dried and bagged for sale.

The precious metals

Recent practice and progress in regard to the treatment of gold ore on the Witwatersrand was reviewed by Andrew King[39] who states that although few major changes have been made in recent years increased attention is being given to ease of operation, maintenance and control with, of course, labour-saving devices. The use of concrete for bins, conveyor gantries, collecting tanks, etc. is increasing.

The treatment of the refractory gold ores of Southern Rhodesia, where the conditions vary greatly in regard to the mineral composition of the ore-bodies, was reviewed by W. G. Vowles.

The largest class of refractory ores are those containing arsenopyrite and these generally need roasting. Successful treatment depends upon efficient concentration before that operation. Flotation has largely replaced gravity concentration.

The refining of gold and silver was surveyed by A. E. Richards.[40] A useful summary is given of the Miller or 'chlorine' process by which the bulk of the world's output of gold is now refined, in particular, of course, that of South Africa. The refining of silver, on the other hand, falls largely within the province of electro-metallurgy.

H. Gordon Dale[41] also contributed a paper on the precious metals to the Symposium in which he dealt with recovery from valuable by-products and scrap, rather than with basic methods of extraction. Some useful notes were added regarding the refining of the platinum metals.

The difficult problem of the treatment of manganese–silver ores was investigated by S. F. Ravitz[42] and others. Tests were made of the dithionate process for effecting recoveries.

W. H. Dennis[43] reviewed the methods now employed in silver extraction.

G. Chad Norris[44] contrasted the former practice at the Amalgamated Banket Areas (Gold Coast) by which gold was concentrated by straking, with that now adopted, using jigs in the primary classifier circuit and the somewhat neglected 'Johnson' concentrator in the secondary circuit; this machine was originally used on the Rand. The change-over was prompted largely by the need for greater security, and this has been achieved. The pulp, of course, is finally subjected to cyanidation.

Aluminium

Published accounts of matters relating to the production of aluminium during 1949 were chiefly concerned with sources of supplies of bauxite,[45] with the production of alumina, and with the refining of the metal itself. Accounts appeared of deposits of bauxite occcurring in the Eastern countries[46] (Palau, Indonesia, Malaya, Indo-China, China and India itself) with notes regarding existing plants and others that are under consideration. An authoritative description of the operations at the

British Aluminium Co's plant[47] at Newport appeared, covering in detail the stages of the Bayer Process.

The practice at various Japanese plants in regard to the extraction of aluminium was issued by the U.S. Bureau of Mines,[48] and the Hungarian Aluminium Industry[49] was also reviewed.

P. Remy-Genneté[50] has studied the question of the production of alumina from high-silica bauxites and finds that the best results are obtained by the reactions with lime in the solid state.

W. Fulda[51] discussed the use of more dilute soda solutions in treating bauxite and the effects of variations in temperature, pressure and duration of treatment on the yield of alumina.

Papers also appeared on the ammonium sulphate process for the extraction of alumina from clay,[52] on newer processes for extracting alumina[53] and on the fundamentals of the economic processing of red mud.[54] A new process for the reduction of aluminium was reported from the United States.[55]

The technique of refining was reviewed by J. Waddington,[56] the catalytic distillation by P. Gross,[57] and a new type of Söderberg Electrode system which simplifies the operation of aluminium furnaces was described by H. Christiansen, junr., and B. Ydstie.[58]

Magnesium

C. J. P. Ball[59] traced the vast amount of progress made in extraction in recent years; much of this, of course, relates to electro-deposition, and a comparison is made of British and American methods. The thermal reduction processes, from which so much had been hoped, have not so far yielded the economic advantages expected of them. The three processes which have been developed, i.e. those of carbide of calcium reduction, of ferro-silicon reduction, and of carbon reduction, have nevertheless provided much useful technological knowledge and experience.

With regard to the thermal reduction of magnesia by ferro-silicon, L. M. Pidgeon,[60] whose name is identified with this process, and J. A. King contributed a paper on the vapour pressure of magnesium to the Symposium of the Faraday Society in 1948.

E. F. Emley[61] gave a detailed account of the procedure in refining magnesium which has been adopted by the Magnesium Electron Company.

Consideration was given to the methods and mechanism by which fluxing refinement is effected, to chemical purification (both by direct exchange with fluxes and by precipitation processes), to de-gassing, to grain refinement, and to the problems presented by the presence of zirconium.

Some of the less common metals

The brief notes and references in this section relate to metals of increasing industrial importance which until comparatively recent years were only produced on a small scale but which now rank among those of considerable annual tonnages. The tendency has been, however, to regard metals such as manganese, chromium, tungsten, molybdenum, vanadium and even titanium, tantalum and niobium, which are largely

marketed as ferro-alloys, as coming within the scope of ferrous metallurgy. Their uses, however, are by no means confined to that sphere. T. F. Smeaton[62] gave an account of the preparation of tungsten for the special purposes of electronics and carbide products, and the growing importance of zirconium is reflected in the number of papers which have appeared recently. G. L. Miller[63] described the production of ductile zirconium by the Murex Company and T. Burchell,[64] of the same company, reviewed the aluminothermic processes of reduction with special reference to the preparation of commercially pure chromium, manganese and the ferro-alloys of niobium and of tantalum.

A. R. Powell[65] described in detail the refining of bismuth derived from the crude by-products of lead and copper smelters. Gulbrausen and Andrew[66] have studied the kinetics of reactions of Ti and of Zr with O_2, N_2, and H_2.

F. S. Wartman[67] describes the reduction of titanium by magnesium from $TiCl_4$ at 800–900° C. in an iron vessel and in an atmosphere of helium. Isera, Shaler and Wulff[68] describe a similar reduction of tantalum by magnesium from $TaCl_5$; *see also* various other papers.[68–76]

Considerable interest has continued to be shown in the metals titanium and zirconium. Titanium has been the subject of two symposia held in the United States,[77,78,79] at which papers were presented dealing at length with work being carried out on alloys, mechanical and physical properties, corrosion resistance and working. Present American production has been stated to be 200 lb. per day,[80] and Du Pont have claimed to be producing over 100 lb. per day and casting ingots up to 400 lb.[81] Remington Arms Company have marketed sheet and rod.[82] The Allegheny–Ludlum Steel Corporation has also entered the titanium market and is reported to be producing 65-lb. ingots with 400-lb. ingots an early prospect.[83]

There appear to have been no major changes in the methods of production, although the Dominion Magnesium Company of Canada have claimed to be producing titanium direct from the oxide[84]; no technical details of this process have been published. Further information on the Kroll process—the reduction of titanium chloride by molten magnesium—has become available,[85,86] and the Battelle Memorial Institute have been working on a modification of this process,[87] whereby continuous production is claimed. Liquid magnesium is added continuously to a titanium chloride atmosphere in a reaction chamber at 760–875° C. The reaction product, consisting of magnesium chloride (liquid) and titanium (solid), runs from the chamber to an arc furnace, where the metal is melted and the chloride, with any excess magnesium, is volatilized, condensed and removed from the furnace, while the titanium is continuously withdrawn from the bottom of the furnace.

Zirconium has continued to be produced by similar methods, namely the reduction of gaseous zirconium chloride by molten magnesium and the dissociation of zirconium iodide on a hot filament. Although commercial production has been limited almost entirely to the former method, the latter is the most desirable when high-purity metal is required for research purposes.

No satisfactory refractory material has yet been discovered for melting titanium and zirconium. Kroll and Gilbert[88] have shown that zirconium can be melted successfully in H.F., arc or split-tube graphite resistor furnaces. The last is preferred for vacuum fusion but the other two are adaptable for melting in an inert gas. Thoria has proved a good crucible material and beryllia is only slightly attacked. Graphite has been used as a crucible material for both metals, although carbon contamination does occur. For zirconium, about 0·10–0·15% carbon is reported,[89] and up to about 0·5% for titanium.

Some of the rarer metals

Alan R. Powell[90] reviewed problems in the production of some of the rarer metals ; he classified the methods which have been investigated for the production of these metals in four main groups : (i) Electrolysis from aqueous solutions (ii) Electrolysis from fused electrolytes (chlorides or fluorides) (iii) High-temperature reduction processes and (iv) Thermal dissociation methods. He reviews the application of one or other of these methods to the particular cases of Ga, In, Tl, Cs, Re, Li, the rare-earth metals, Ge, Re, V, Ti, Zr, Th, and Va.

The rare-earth industry, with particular reference to cerium and other products of monazite, was reviewed by H. E. Kremers,[91] the production of thorium by W. Espe[92] and of indium by R. Kleinhert.[93]

References

1 Fourth Empire Congress of Mining and Metallurgical Institutions, July, 1949
2 Symposium on Refining, Inst. of Min. and Met., July, 1949
3 Symposium on the Physical Chemistry of Process Metallurgy, Faraday Society, London, 1948
4 Congress on Non-Ferrous Metallurgy: Assocn. des Ingénieurs sortis de l'École de Liège, 1947 (Published by A. I. Lg. Quai Paul Van Hoegaerden 12, Liège, Belgium, 1949)
5 Lajeunesse, R. S., *Metal Ind., Lond.*, 1949, Oct 14, 342
6 Mineral Development Committee (H.M.S.O., 1949)
7 E.R.P. Report of the (O.E.E.C.) Non-Ferrous Metals Committee (H.M.S.O., 1948)
8 Colonial Primary Products Committee, Metals and Minerals Panel Report (H.M.S.O., 1949)
9 Boggs, W. B., 'Some Modern Developments in Copper Pyrometallurgy,' Fourth Empire Mining and Metallurgical Congress, London, July, 1949
10 Miller, H. J., 'The Fire Refining of Copper,' Symposium on Refining of Non-Ferrous Metals, Inst. Min. Metall., London, July, 1949
11 Bauld, R. H., 'Trends in Methods of Refining and Casting for High Conductivity Copper, *ibid.*, July, 1949
12 Friggens, W. J., Page, E. W. and Milligan, T., 'The Electrolytic Copper Refinery of the Rhodesia Copper Refineries Ltd.,' *ibid.*, July, 1949
13 Trumball, R. C., Hardick, W. and Lawford, E. G., 'Notes on the Treatment of Pyritic Cinders at the Plant of the Pyrites Co. Inc., Wilmington, Delaware,' *Bull. Instn. Min. Metall.*, 1948, No. 505 (Dec.); 1949, No. 507 (Feb.)
14 Potts, H. R. and Lawford, E. G., 'Recovery of Sulphur from Smelter Gases by the Orkla Process at Rio Tinto, ibid., 1949, No. 509 (April); 1949, No. 511 (June)
15 Baker, W. A. and Hallowes, A. P. C., 'Experiments in the Removal of Selenium and Tellurium from Blister and Fire-Refined Copper, ibid., 1949, No. 513 (Aug.) and Nos. 515 (Oct.) and 516 (Nov.)
16 Daniell, L. L., 'The Morenci Smelter, Arizona,' *J. Metals, N.Y.*, 1949, **1** (Jan.)
17 Peretti, E. A., 'An Analysis of the Converting of Copper Matte,' *Discuss. Faraday Soc.*, 1948

[18] Emert, Oskar, 'Operations at the Duisburg Copper Smelter' (Application of Metal Amalgams), *Z. Erzbergb.*, 1949, **2** (Feb.)
[19] Fitzpatrick, W. S., 'The Economic Utilization of Waste Gases by the Integration of Base Metals and Chemical Fertilizer Operations at Trail, B.C.,' Fourth Empire Min. & Met. Congress, London, 1949
[20] Green, F. A., 'Lead Sintering Practice at Port Pirie (South Australia),' *ibid.*, 1949
[21] Green, F. A., 'Refining of Lead and Associated Metals at Port Pirie (South Australia),' Symposium on Refining, Instn. Min. Metall., London, July, 1949
[22] Collins, A. G., 'Effect of High Copper-Content in Lead Blast Furnaces,' *J. Metals* (*N.Y.*), 1949, 347
[23] Isbell, W. T., *J. Metals, N.Y.*, 1949, **1** (ii), No. 3, 81
[23a] Hanley, H. R., *J. Metals*, 1950, **188**, 16 G
[24] Fusland, R. R. and Wertz, D. H., *J. Metals, N.Y.*, 1949, **1**, 393
[25] Bunce, E. H. and Peirce, W. M., *Engng. Min. J.*, 1949, **150**, 3, 56
[26] Smith, G. T. and Moyer, R. C., *J. Metals, N.Y.*, 1949, **1**, 360
[27] Feddersen, P. C. and Lee, H. E., ibid., 110
[27a] Robson, S., Symposium on Refining, Inst. Min. and Met., July, 1949
[28] Jones, E. H., 'Refining of Tin,' Symposium on Refining, Instn. Min. Metall., July, 1949
[29] 'New Tin Smelting Projects in the U.S.A.,' *Min. J.*, 1949, No. 327
[29] 'Tin Research,' ibid., 1949, No. 461
[30] Malan, H. L., *Min. Mag., Lond.*, 1949, **81**, 137
[31] Mantell, C. L., 'Tin,' 2nd Ed., 1949 (New York: Reinhold Pub. Corpn.)
[32] Griffiths, Sir William, 'The Nickel Industry: Twenty Years on,' Fourth Empire Congress, London, 1949
[33] Queneau, P., *Trans. Canad. Instn. Min. Met.*, 1948, **51**, 356
[34] Young, Roland S., 'Cobalt' (American Chemical Society Monograph) (Reinhold Pub. Corpn., 1948). (Reviewed in *Bull. Instn. Min. Metall.*, 1949, No. 514, Sept.)
[35] Bryant, P. S., 'Cobalt Refining,' Symposium on Refining, Inst. Min. & Met., London, July, 1949
[36] Talbot, H. L. and Hepker, H. N., 'Investigations on the Production of Electrolytic Cobalt from a Copper–Cobalt Flotation Concentrate,' *Bull. Instn. Min. Metall.*, 1949, No. 514 (Sept.)
[37] Wells, H. R. *et al.*, 'Concentration of Copper–Cobalt Ores, Idaho,' U.S. Bur. Mines, 1948, Rep. Invest. 4279; *Brit. Abs.* B.I, 1949 (May)
[38] Symons, Ralph, 'Mining and Milling Antimony Ore at the Consolidated Murchison Goldfields, Transvaal,' *Bull. Instn. Min. Metall.*, 1949, No. 506 (Jan.)
[39] 'Mineral Dressing and Cyanidation in Southern Africa,' Fourth Empire Congress, 1949, Paper No. G.2, Ed. Philip Rabone; (Gold Ore Treatment by Andrew King)
[40] Richards, A. E., 'The Refining of Gold and Silver,' Symposium Instn. Min. Metall., London, 1949
[41] Dale, H. Gordon, 'The Precious Metals,' *ibid.*
[42] Ravitz, S. F. *et al.*, 'Treatment of Manganese–Silver Ores,' U.S. Bur. Min. Tech. Paper 723, 1949
[43] Dennis, W. H., *Min. J., Lond.*, April 9, 1949, 232
[44] Norris, G. Chad, 'Gold Concentration at the Amalgamated Banket Areas Reduction Plant,' *Bull. Instn. Min. Metall.*, 1949, No. 516 (Nov.)
[45] 'Sources of Bauxite in Asia,' Mineral Trade Notes Supplement, 1948, No. 27 (Jun.)
[46] Jain, S. C. and Paut, P. D., 'Production of Aluminium from Indian Bauxite,' *Trans. Indian Inst. Met., Calcutta*, 1949, April
[47] 'Alumina by the Bayer Process' (British Aluminium Co.), *Industr. Chem. chem. Mfr.*, 1949, Sept., 431
[48] 'The Japanese Aluminium Extraction Industry,' U.S. Bureau of Mines Inf. Circ. 7496, 1949
[49] Bandart, G. A., *Rev. Alumin.*, 1949, **26** (154), 110
[50] Remy-Genneté, P., *Chim. et Industr.*, 1948, **60** (4), 336
[51] Fulda, W., *Metall*, 1948, No. 23/24, 397
[52] Seyfried, W. R., 'The Ammonium Sulphate Process for the Extraction of Alumina from Clay at Salem, Oregon,' *Metals Tech.*, Dec. 1948; A.I.M.E. Tech. Pubn. 2473

[53] Bücke, K., *Arch. Metallk.*, 1949, **3** (6), 208
[54] 'Fundamentals of the Economic Processing of Red Mud,' *Metall*, July, Aug. 1949 (In German)
[55] 'A New U.S. Aluminium Reduction Process,' *Mining J.*, 1949, T. 27
[56] Waddington, J., 'Refining of Aluminium,' Symposium on Refining, I.M.M., London, 1949
[57] Gross, P., 'Catalytic Distillation of Aluminium,' *ibid.*
[58] Christiansen, H., junr. and Ydstie, B., 'The Söderberg Electrode System,' *J. Iron Steel Inst.*, May, 1949
[59] Ball, C. J. P., 'Extraction, Alloying and Fabrication of Magnesium,' Fourth Empire Congress, July, 1949
[60] Pidgeon, L. M. and King, J. A., *Discuss. Faraday Soc.*, 1948, No. 4, 197
[61] Emley, E. F., 'The Refining of Magnesium,' Symposium on Refining, Instn. Min. Metall., July, 1949
[62] Smeaton, T. F., 'The Preparation of Tungsten for Special Purposes,' Symposium on Refining, Instn. Min. Metall., July, 1949
[63] Miller, G. L., 'The Production of Ductile Zirconium,' *ibid.*
[64] Burchell, T., 'The Aluminothermic Process of Reduction,' *ibid.*
[65] Powell, A. R., 'Refining of Bismuth,' *ibid.*
[66] Gulbransen and Andrew, 'Kinetics of Reactions of Ti and of Zr with Oxygen, Nitrogen and Hydrogen,' *Metal Trans. N.Y.*, 1949, **185**, 741
[67] Wartman, F. S., *Metal. Progr.*, 1949, **55**, 188
[68] Isera, Shaler and Wolff, 'Tantalum Powder,' Amer. Inst. Min. Metall. Eng. Tech. Paper 2277
[69] Starliper, A. G., 'Titanium Metallurgy,' *Met. Trans., N.Y.*, 1949, **185**, 785
[70] Kenworthy and Knickerbocker, 'Titanium Investigations,' ibid.
[71] Barksdale, 'Titanium Technology and Chemistry,' *ibid.*
[72] Worner, H. W., *Chem. Engng. Min. Rev.*, 1948, **40**, 254
[73] Lee, J. A., *Chem. Engng.*, 1948, **55**, No. 9, 110, 152
[74] 'Melting and Casting of Zirconium,' *J. electrochem. Soc.*, 1949, **96**, 158
[75] 'Zirconium as of 1949,' *J. Metals, N.Y.*, 1949, July 6
[76] Patal, 'Vanadium from Bauxites and Ferro-Vanadium,' *Brit. Abs.*, 1949, B.I, (Jan.)
[77] *Metal Progr.*, 1949, **55**, 185, 252, 254, 345, 398, 400
[78] U.S. Dept. of the Navy, Office of Naval Research, Titanium Symposium, Dec. 16, 1948
[79] Amer. Chem. Soc. 116th Meeting, Atlantic City, Sept. 18–23, 1949
[80] Ralston, O. C., *Sheet Metal Industr.*, 1949, **26**, 2132
[81] *Amer. Metal Market*, Sept. 22, 1949
[82] *Fortune*, 1949, **34** (5), 121, 126, 128
[83] *Amer. Metal Market*, Aug. 13, 1949
[84] Kopecki, E. S., *Iron Age*, 1949, **163**, 221
[85] Wartman, F. S., *Metal Progr.*, 1949, **55**, 188
[86] U.S. Bur. of Mines, R.I. 4519, Aug. 1949
[87] *Prod. Engng.*, 1949, **20**, 130
[88] Kroll, W. J. and Gilbert, H. L., *J. electrochem. Soc.*, 1949, **96**, 158
[89] Hayes, E. T., Dilling, E. D. and Roberson, A. H., A.S.M. Preprint, 1949, No. 32
[90] Powell, A. R., 'Some Problems in the Production of Rarer Metals,' Symposium on Refining, Instn. Min. Metall., July, 1949
[91] Kremers, H. E., 'The Rare-Earth Industry,' *J. electrochem. Soc.*, 1949, **96** (Sept.)
[92] Espe, W., *Pwdr. metallurg. Bull.*, 1949, **4**, 17
[93] Kleinhert, R., 'Indium from Rammelsberg Ore,' *Z. Erzbergb.*, 1949, **2** (Jan.)

ELECTROCHEMICAL AND ELECTROMETALLURGICAL INDUSTRIES

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In the present report the order has been somewhat altered compared with that of previous years so that electrodeposition is first dealt with, followed by electrorefining and electropolishing. A brief section on matters concerned with condensers and dielectrics which appear to be of chemical interest is then followed by the section on cells. Any such division is arbitrary: this one appears to be theoretically logical.

Electrodeposition

(i) *General*

An extensive discussion of metallurgical aspects of electrodeposits[1] deals with grain size and structure, porosity, mechanical properties and adhesion of deposits. Impurities of Fe, Cu and Zn to the extent of 10 p.p.m. are found to increase the stress in deposits, particularly at high p_H. A method is given for calculating the internal stress of deposits from the curvature of a plated strip which corrects for stress relief due to curvature and for stress caused by temperature changes in the bi-metallic strip. A second review[2] deals with the determination and significance of the physical properties of electrodeposits.

Metal plating on non-conductors is a subject of growing importance and it has been reviewed by C. A. Marlies.[3] It is found to be impractical to use baths which run hot or produce much gas and a small current-density is advisable at the commencement of electrolysis, and the baths should be neither strongly acid nor strongly alkaline. The covering used to allow conduction on the surface of the non-metal is usually graphite, bronze or chemically reduced Ag. The film layer must be less than 0·001 in. in thickness to ensure satisfactory adhesion and for satisfactory strength it should be greater than 0·003 in. Between 0·001 and 0·003 in., the film strength and stiffness are very low so that blistering and splitting of the material occurs. A review by J. Fischer[4] on the configuration of plating baths might profitably be read in connexion with the account mentioned above, and also the interesting summary by E. Mehl[5] on the separation of films used in electro-forming. These films are divided by this author into the following groups: mechanically applied films of oil, wax or graphite; films produced by chemical or electrochemical alteration of the mould surface, including oxide, sulphide, selenide, chromate and iodide films; plated films (usually chromium); films on permanent moulds such as the oxide films on Cr and Cr–Ni steels. The important factors in stripping electro-formed coatings include mould design, mould finish and strength of deposit.

Powder metallurgy has recently become increasingly important and the plating of pressed metal powder parts is a field which should receive

increasing attention. A description of the methods[6] of plating with Cu–Ni–Cr and Ni–Cr on 85–15 brass powder with 0·5% Zn stearate is given. The principal difficulty is retention in pores. To overcome this, the use of neutralizing dips and alternate hot and cold rinses is suggested. The corrosion resistance of plated compacts is comparable to that of plated massive metal parts.

Finally, an interesting technical improvement in the production of carbon electrodes may be noted.[7] They are prepared by pouring a mixture of powdered carbon and binder into moulds and subjecting the mixture to high-frequency vibrations before baking and igniting. The product has a higher density, and possesses better physical strength, stability and improved electrical conductivity.

(ii) *Individual metals*

Aluminium.—In a new patented process for the production of Al,[8] the aluminium fluoride melt is circulated cyclically through a series of cells, the Al_2O_3 content of which decreases from 12–14% to 2–2·5% before replenishments. The Al from the series of cells with lower Al content is relatively pure. Fe is recovered in association with coke in the initial cells and Si and Ti are also eliminated there. Either alumina or bauxite ores can be used. The decomposition of the Fe, Si and Ti contents of the Al by recovering them in the form of an Fe alloy is carried out by filtering the replenished fluoride melt through a carbonaceous filter, treated with Al and filtered again before being passed to the first of the electric cells. In a complementary paper,[9] the reactions of Al_2O_3 dissolved in AlF_3, cryolite, NaF and Na_2O are discussed. The optimum voltage, temperature, electrical conductivity of the bath and current density (c.d.) in these processes are critically discussed.

The detail of methods for the electroplating on Al for aircraft components (including the zincate treatment) have also been reported.[10]

Copper.—The advantages and disadvantages of the usual copper sulphate and cyanide baths are described by J. Salauze.[12] Of the more recent developments, some of the most interesting have been investigated by K. S. Willson and W. G. Ellis[13] who find that acyl thiophen as an addition agent in a cyanide bath yields a fine bright Cu plate. Agitation causes a brighter plate to be produced and allows the use of higher current densities up to 60 amp./ft^2. Interruptions or reversal of the current, and the use of a.c. superimposed on d.c., improved the brightness of the deposit. The concentration of the addition agent should be at least 0·1 g./l. and preferably up to 2·5 g./l. Other, cheaper compounds, e.g. benzoyl thiophen, are suggested and corresponding conditions given. Acetyl cyanamide has been used by H. Brown[14] for a similar purpose, namely to increase the lustre of the copper deposits and decrease the grain size without lowering the ductility of the plate. Only 0·1–0·2 g./l. of acetyl cyanamide is added to the standard acid copper-plating bath which may be composed of $CuBF_4$, NH_4BF_4 and HBF_4 (temperature 50–75° F.). The bath is vigorously agitated and the c.d. used is between 10 and 100 amp./ft^2. Partially hydrolysed gelatin in small quantities (0·1 g./l.) improves brightness, but decreases ductility.

The little-understood role of colloids (particularly from cellulose and

gelatin) in the copper-plating bath is discussed by E. Vuiguer[15] with special reference to the prevention of the growth of trees and nodules.

Chromium.—The effect of temperature and high frequencies on the electrodeposition of chromium has been recently examined. M. G. Herbach and C. W. Bowden claim[16] that temperature is the most critical variable in hard and decorative Cr plating; they describe a simple control system applicable to heating the bath using steam. Superimposed high-frequency a.c.[17] was found to reduce the efficiency of the deposition. This was confirmed in the case of Ni and Cr plating.

The structure of thick Cr deposits has been investigated[18] in relation to the effect of lowering of bath temperature, decreasing the sulphate ratio, increasing the c.d. above 55° c. and decreasing it below 55° c. These operations are all found to cause refinement of the crack pattern of Cr deposits developed by anodic etching. The effect of H_2SO_4 content upon the structure of hard Cr coatings shows[19] that hard Cr can be deposited from baths having more than 1·2% H_2SO_4. Higher bath temperatures and c.d's. have to be used when the H_2SO_4 concentration is higher.

A remarkably extensive investigation of the wear-resisting characteristics of Cr plate is reported by Ichizo and Iitaka from Tokyo.[20] The amount of wear of a test piece is expressed by the reduction in weight when it was rubbed for 20 min. by a revolving drum of a nitrided steel aeroplane cylinder. Cr plates made under different conditions were measured for the relative amount of wear, the results being 0·15–0·9 mg./20 min./0·2 cm². for hard plates and 0·1–0·4 mg./20 min./0·2 cm². for soft plates. It is of considerable interest to note that some soft plates, though of thickness 0·013 mm., i.e. less than half that of the hard plates, retained their wear resistance for the same time as the hard plates. The bright Cr plate showed a poor wear resistance; this was ascribed to the thinness of the deposit. Various metals[21] e.g. Ag, Cd, Ni, Fe, were plated on steel as a basis followed by Cr, and in another series of experiments Cr was directly plated on metal plates. From these experiments it is concluded that the wear-resistant characteristics of Cr are based upon its own properties developed during electrodeposition and not upon the mutual relation established with the base metal. The high H content of crystalline chromium is not an important factor in the wear-resisting characteristics of Cr.[22] Thus, all H in the plated Cr is practically removed at 500° c., whereas abrasion became significant at 650° c.

It has been found[23] that the direct plating of Cr on to Al or Al alloys can be accomplished by roughening the surface without the use of intermediate layers. The chromium adheres mainly by mechanical interlocking so that complete absence of oxide films is not essential. The method entails dipping the article into a 10% caustic solution at 65° c. Heavy metals present in the alloy produce a dark film on the surface. The high potential between the finely divided heavy metals and the basic material results in a uniformly rough surface and the adhesion of the deposit is good enough to allow the bending of thin sheets without spalling. Use of an intermediate layer is also possible. The article is then pickled in an alkaline bath containing Zn and Fe; a dull grey film is formed and removed by rinsing in H_2SO_4 and HNO_3. A thin Cu coating is then

applied in a conventional cyanide bath. Cr is plated immediately over this Cu film which may be so thin as to be undetectable under the microscope. A somewhat different method for obtaining hard Cr layers upon light alloys has been developed by J. Patrie.[24] Well adhering layers of Cr of 20 μ. to 0·1 mm. thickness are produced by first pickling the light metal in a solution of 400 g./l. of NaCl, 2% HF, 4% H_3BO_3 at 25–30° c. for about 1 min. and then plating in a bath of 250 g./l. chromic anhydride and 1·25–2·5 g./l. H_2SO_4. The ratio of CrO_4 ions to SO_4 ions must be greater than 100. The deposits have the best adhesion when made at 50–60° c. at a cathodic c.d. of 40 amp./dm^2. During the initial period of electrolysis, however, the c.d. should be 60–80 amp./dm^2. until a uniform thin film of Cr is deposited.

Hard chrome plating on tools and machines is reviewed by W. F. Troescher.[65] Two main processes are used: (1) bright Cr plating and (2) hard Cr plating. The latter can be deposited directly on the basic metal in thicknesses of 0·02–0·2 mm. and has a greater wear resistance, lower friction coefficient and more resistance to high temperatures. The application to various types of tools are described briefly.

A development of Cr plating of aeroplane propeller blades[26] is aimed at avoiding the excessive decrease in fatigue strength by a suitable choice of bath conditions and heat treating. The blade is cleaned in the usual way, with care to avoid hydrogen embrittlement, and is made the cathode in the bath. The concentration of Cr may vary from 500 to 800 g./l. The ratio of the concentration of SO_4 or other anion catalyst to CrO_3 concentration is from 1 to 230. The temperature must be less than 40° c. and the c.d. 1–4 amp./cm^2. The ordinary oven treatment of the blade is for 3 hr. at 260° c.

Fluorine.—It is well known that the production of fluorine from a melt containining KHF_2 involves difficulties of the reaction of F with the anode material. This problem has been examined in some detail.[27] The increase in the potential drop across the cell during the electrolysis is caused by a deposit of a soot-like spongy mass identified as $(CF)_x$. This layer can now be removed by electrolysis at a higher voltage (40–50v.). The anode effects are associated with (i) a luminous appearance at the anode; (ii) a change in the anode surface; (iii) a change in the composition of the gases evolved at the anode; (iv) a decrease in anode weight; (v) a lowering of the total overpotential.

Lead.—A former difficulty in lead plating was that the use of fluoborate and fluosilicate baths has involved marked corrosion. Former attempts to deposit Pb from alkaline baths have produced a strongly non-adherent metal. A new invention[39] contains the formula of a suitable bath from which the lead can be satisfactorily deposited. The bath consists of a Pb salt, NaOH, Rochelle salt and addition agents. It has a long life, better throwing power than acid baths, and the nature of the deposits can be favourably compared with acid baths. As an alternative non-corrosive bath for Pb plating it is possible to use[40] a Pb plating solution which does not contain fluorine compounds and which eliminates the necessity of a preliminary Cu plate on ferrous articles. This consists of an aqueous solution of Pb acetate, bone glue and a water-soluble aromatic

sulphonic acid. The conditions for plating are 120–160° F., 50–150 amp./ft^2. and agitation.

Magnesium.—The invention of a cell for Mg production from a fused salt mixture specially adapted for long lasting operations is claimed by R. D. Blue, R. M. Hunter and M. P. Neipert.[28] A sufficient number of bipolar electrodes in one or more electrolytic zones are connected to a single chamber for collecting the metal and feeding in fresh salt. The electrodes are below the surface of the bath and protected from contact with free chlorine.

Molybdenum.—It has now been found possible[29] to electrodeposit Mo from aqueous solutions of MoO_3 which contain high concentrations of salts, formates, acetates, propionates, fluorides and phosphates of Na, K and NH_4. The optimum p_H range for this deposition is 5·5–6·8, the c.d. range 0·06–3·3 amp./cm^2. and the temperature 30–55° C. Deposits on Cu, Ni and Fe cathodes have been obtained with Pt or C anodes. Co, Ni and Fe were co-deposited with Mo from solutions containing salts of these metals.

Nickel.—The physical properties of electrodeposited Ni have been made the subject of an A.E.S. Research Project.[30] The effect of solution composition and operating variables on the physical properties of Ni plate have been studied, baths with additions of Na_2SO_4, $(NH_4)_2SO_4$, HCl and Ni $(AcO)_2$ being used. The effects of p_H, temperature, c.d. and thickness of deposit were studied in relation to hardness, tensile strength, elongation, Young's modulus, fatigue strength, electrical resistivity and magnetic properties. The porosity of electrodeposits of nickel has also been investigated.[31] A high pressure (about 1 atm.) is maintained constant on one side of the foil and the rate of increase of pressure on the other (low pressure) side is measured. The results of this method of investigation of porosity agree with those of previous investigations at lower pressures. Sound wrought Ni foils 2·5 μ. thick are far less porous than electrolytic foils of comparable thickness. Ni deposits having a preferred orientation of (110) crystal faces parallel to the base metal surface were found to be more porous than those with (100) faces parallel.

The quality of the bond between electrodeposited Ni and a Ni surface, particularly a Ni 'starter sheet,' is improved[32] by dipping the Ni surface in an aqueous acid–chloride bath containing Cu ions. After immersion for about 5 min. at 80° F., the surface is rinsed with water and transferred to the plating bath. Compressed air is passed through the bath at a rate sufficient to keep the copper in a fully oxidized state.

An interesting semi-bright Ni plating process has been recently described by K. S. Wilson and A. H. Du Rose,[33] the process having the advantage that the surface irregularities are filled in. The deposit requires only a light pressure on the colour buffing wheel to bring out the full brightness. It is intermediate in hardness between grey and bright Ni. The $NiSO_4$ concentration is 40–45 oz./gal.; $NiCl_2$ and H_3BO_3 are present at 6 oz./gal.; the operating temperature is 120–135° F.; p_H = 3·5–4·5 and about 0·75 to 1·0 lb./100 gal. of water of addition agent should be present.

For bright plating of Ni and Co, the most useful conditions would be to

produce a smooth, bright plate in a short time, i.e. at high c.d. A method of doing this while maintaining the ductility of the plates is now available.[34] The cathodic current flows for 2 sec. or less and the anodic for $\frac{1}{2}$ to $\frac{1}{25}$ sec. The total quantity of electricity (in coulombs) with the specimen as anode should be 4–60% of that with the specimen as cathode, but the c.d. need not be the same in the two directions. The c.d. may be 100–500 amp./ft^2. of cathode area so that plating can be carried out in about 20% of the usual time. The process is probably successful because periodic reversal causes inferior metal, e.g. nodules, to be preferentially removed, giving a smoother plate. The corrosion resistance of the plate is increased compared with ordinary nickel plate; it is brighter, smoother and ready for Cu plating without buffing. A feature of the process is that better results are obtained with irregularly shaped cathodes. The paper records eight solutions which can be used in the process.

The need for a method for the plating of Ni on Al[35] is supplied by use of a 5–20% solution of NH_4HF_2. The Al alloys are predipped in a 5–20% solution of the fluoride and are then anodically oxidized in 5–20% H_3PO_4 at a 4-v. potential. It is finally electroplated in a bath having p_H below 6.

J. G. M. Brenner[36] has found a valuable catalytic effect in Ni and Co plating by chemical reduction with sodium hypophosphite, deposition only occurring in the presence of certain metals immersed in solution. The mechanism in alkaline solutions is represented by the following reactions:

$$Ni^{++} + M = Ni^{+} + M^{+}$$
$$OH^{-} + M^{+} = OH + M$$
$$2Ni^{+} = Ni^{++} + Ni$$
$$H_2PO_2^{-} + 2OH = H_2PO_3^{-} + H_2O.$$

The over-all reaction is:

$$Ni^{++} + H_2PO_2^{-} + 2OH^{-} = Ni + H_2PO_3^{-} + H_2O.$$

Thus, according to this mechanism the metal surface plays the role of a source and sink of electrons. In acid solutions

$$H_2PO_2^{-} + M = H_2PO_2 + M^{-} \quad \ldots\ldots\ldots \quad (A)$$

and the over-all reaction is

$$H_2PO_2^{-} + Ni^{++} + H_2O = H_2PO_3^{-} + Ni + 2H^{+}.$$

This mechanism differs from that in alkaline solution by the type of union first responsible for the electron-transfer step at the metal surface, i.e. reaction (A). It is of interest to note the theoretically unexpected fact that in mixed Ni–Co acid solutions only Ni is precipitated.

Some novel work showing considerable technological potentialities concerns the use of atomic hydrogen in obtaining brighter and more highly stressed Ni deposits.[37] These are obtained in simple sulphate baths (e.g. $NiSO_4$, 100; $MgSO_4$, 20; NaCl and H_3BO_3 15 parts) by polarizing one face of the cathode in H_2SO_4. On the other side of the cathode, isolated from the H_2SO_4 side, and immersed in $NiSO_4$, this produces finer, brighter and more highly stressed deposits. The addition of a trace of SeO_2 to the H_2SO_4 increases the effect which then spreads

over the whole of the surface of the cathode, including parts not subjected to the evolution of hydrogen. Again it cannot be explained theoretically why these effects are wholly absent in the deposition of copper.

Selenium dioxide has also been found to have a general brightening effect on nickel plate, so long as high c.d.'s are used.[38] The best conditions are obtained at p_H 5·74 at a temperature of 17° c. and constant SeO_2 content of 0·1 g. The internal stresses in the Ni are distinctly higher than with the addition of, say, $CdCl_2$ (0·3 g./l.). It is probable that the effect of SeO_2 is to favour occlusion of hydrogen in the deposit.

Niobium and tantalum.—In an older paper which has recently become available,[11] a report is given of the electrolysis of complex organic salts of Nb or Ta in order to obtain a deposit of Ta or Nb on cathode materials.

Rhenium.—A general study[41] has been made of the quantitative aspects of rhenium deposition, with special reference to current efficiency. Re is plated as a shiny, white, adherent, metallic, cathodic deposit from several different types of aqueous baths. The current efficiency, however, is low, i.e. some 15–1%. The H_2SO_4 bath was found to be the most successful; a new citric acid bath is also described.

Rhodium.—Rhodium plating[41] gives a decorative finish which possesses a particularly high and relatively constant reflectivity, resistance to heat and abrasion, and complete resistance to corrosion.

Silver.—W. E. Hesselberger[43] describes the operation of a fully automatic and a semi-automatic silver-plating bath. The compositions of the solutions used are given and the method of controlling them is discussed in some detail.

Tin.—The use of polydioxalane in obtaining dense, adherent and bright Sn electroplates has been described by A. G. Gray, W. F. Gresham and D. J. Loder.[44] The agent is effective in acid and alkaline solutions but the best effect is in the recently developed neutral baths. An improved effect is obtained if the polydioxalane has a multiplicity of aliphatic ether groups.

Tantalum.—H. J. Seim and M. L. Holt[45] have reviewed initially the deposition of Ta from aqueous and non-aqueous solutions. Experimental work did not confirm the success of any of the proposed methods. Other baths tried were also unsuccessful, although the possibility of deposition from fused baths is not yet excluded.

Zinc.—A general discussion of the problem of Zn plating, covering, cleaning, types of baths used, procedure and passivation is given by R. Mansell.[46] A. E. Chester and F. Reisinger[47] have continued the investigation of the use of complex organic compounds upon deposition rates and find that brighter Zn deposits can be obtained by addition to an alkali Zn plating bath of a complex formed from piperonylaldehyde and an aldonic acid, preferably gluconic acid. The composition of the mixture is given. In similar work[48] it was found that Zn deposited from a cyanide plating bath gave a white, but not bright, appearance, whereas if the condensation product of sodium cyanamide and formaldehyde is added to the solution the deposit was very bright. Usually, electrolytically refined Zn is of a high purity. Organic additives have now also been used for improving the purity of the specimen.[49] Cresylic acid and pine

oil are added to the solution and the p_H of the latter should be about that corresponding to the equilibrium of the solution with ZnO, i.e. 5·1 to 5·5. The c.d. should not exceed 25 amp./ft^2. and agitation avoided since it transports anode slime to the cathode. Impurities of the order of 0·003% in Zn have been reduced, by the use of this method, to 0·0006%.

The additives in Zn plating may consist of other electrolytes. Thus, additives of Sn up to 5 g./l. to an electrolyte of Zn (in the form of $Zn(OK)_2$) yields dense and light Zn deposits at room temperatures with a c.d. of 0·7 amp./dm^2. as compared with the previously permissible c.d. of 0·2.[50] In the absence of Sn, dense Zn deposits can be obtained from the same electrolyte at 50° c. but the deposits are much inferior to those obtained in the presence of Sn.

A third method of improving zinc deposits is reported from the Chelyabinsk Electrolytic Works, Russia.[51] Careful p_H control facilitated the effective elimination of Fe, Cd, SiO_2, As, and Cl. Co is removed in the solutions returning from leaching Cu–Cd cake after removal of Cd. Pb cooling coils in the electrolytic tanks were advantageously replaced by Al coils.

The corrosion phenomena of zinc are still the subject of controversy. A. E. Anderson[52] has given an informative account of the chemical and physical characteristics of Zn related to understanding and explaining the observed surface phenomena.

Zirconium.—A complex Zr salt prepared by treating $ZrCl_4$ with $(NH_4)_2CO_3$ deposits Zr upon electrolysis.[53]

Alloys.—Some fairly extensive effort in the field of electrodeposition of alloys shows appropriate reward. Thus, Ag–Pt, Pt–Au, Ag–Au and Ag–Pt–Au alloys have been deposited from a solution of the acid chlorides.[54] The deposits were of high quality except those of Ag–Pt–Au which are dark and spongy. Alloys containing up to 50% W may be obtained from electrolytes prepared by dissolving WO_3 in NaoH solution in the presence of tartaric acid, boric acid, and $CoSO_4$. The current efficiency is 35%. The Co–W alloy is harder than pure W; *X*-ray diffraction studies reveal it to be a solid solution.[55] A new U.S. patent[56] indicates the possibility of preparing Pb–Sn–Sb alloys by electrodeposition. Bright cathodic deposits of Co–W alloys have been obtained[57] from a bath containing cobalt sulphate, sodium tungstate and citric acid in the molar ratio of 1 : 1 : 1·5. Anodes of Co or W or of both these metals or of some inert metal can be used. Similar work has been carried out for Fe–W alloys.[58]

Corrosion resistance has been the objective of A. Schaefer and J. Mohler[59] who have prepared Pb–Sb–Sn alloys from a bath containing HBF_4, basic lead carbonate, SbF_3, $SnSO_4$ and gelatin. The electroplates thus obtained are useful both as corrosion resisters and for bearing surfaces. Another corrosion-resisting electroplate has been found in Sn–Zn alloys.[60] It also affords a better basis for paint than Cd plate. For all ordinary purposes the preferred composition range is 75–80% Sn and 20–25% Zn. Corrosion tests in this case show that a Sn–Zn plate of the above composition, not less than 0·0003 in. thick, affords good protection of steel. The anode is a filmed alloy of the same composition as the alloy being deposited.

Electrolytic refining and electropolishing

(i) *General*

A timely review on molten salt electrolysis has been given by J. L. Andrieux[61] with special reference to the preparation of powders. Be, Ti, Zr, Th, Ta, Cb, Cr, Mo, W, U, Mn, Cu, Ag, Fe, Co, Ni and Pt can all be prepared in this way which also aids the refining of Fe and FeW alloys.

One of the best-known workers of recent times in the field of electropolishing, P. A. Jacquet,[62] has written a comprehensive report on this field which deals with the fundamental phenomena accompanying electropolishing. This process is only possible in a medium in which the anodic products of solution have a high solubility. Preparation of the samples, electrolytes used, conditions of electrolysis, temperature, duration of electrolysis, treatment of the surface after electrolytic polishing, etc., are discussed and an extensive bibliography given.

A change of surface brightness with time in the course of anodic solution in H_3PO_4 of $d = 1{\cdot}55$ at 100 amp./dm^2. is reported[63] for Cu surfaces obtained by chiselling, drawing out, abrasion, compression, shearing, and electrodeposition for α-brass surfaces ground by various procedures, for carbon and alloy steel and for duralumin. Anodic solution of specially textured surfaces increases the surface brightness to a striking degree, depending upon the procedure used to obtain the texture.

The chemical colouring of metals remains largely an art, and its extreme usefulness is illustrated by M. C. N. Holt and A. M. Ward[64] who report the colouring of copper and brass in a solution containing $Na_2S_2O_3$, lead acetate and an organic acid or aldehyde. Golden, red, blue, green and grey colours were obtained. The mechanism of these colour formations is unknown but may be connected with the deposition of PbS.

(ii) *Specific elements*

Aluminium.—A new method for the refining of Al has been patented.[65] Crude Al is fused with Cu 30% and Si 2% into an alloy to serve as the anode, which is dipped into a liquid composed of $BaCl_2$, 55%; AlF_3, 23%; NaF, 14%; and MgF_2, 8%. A current of 600 amp. at 70 v. is then passed at 200–230° c. The Al accumulating in the top layer is 99·99% pure. Another patent[66] is concerned with the maintenance of a constant concentration in the melt. Powdered Al is fed from a silo in such a way that there is always a certain quantity of solid immersed in the electrolyte in a side compartment separated from the electrolytic furnace. The gradual melting of Al_2O_3 keeps a constant concentration in the electrolyte.

The anodic oxidation of Al has received considerable attention since the last Report was written. In one process[67] the electrolyte consists of H_2SO_4 (5–95%) and $BeSO_4$ (0·5–5%). The anodization may be carried out with a.c. or d.c. at 12·5 v., c.d. 0·8–1·5 amp. and temperature 16–25° c. The presence of the Be, for reasons not at present clear, produces a more regular anodization, augments the opacity of the oxide coating and renders it more adherent. Very hard oxide layers on Al which are susceptible to colouring are claimed by a method[68] similar to that above. The electrolyte contains H_2SO_4 and Be salts in aqueous solution. In another process,[69] also applicable to the alloys of Al, the polished work

is degreased and given a preliminary chemical treatment in an alkaline bath, p_H 10–12, containing Na_2CO_3 10, Na_2SO_4 10, H_2O 1–5, alkali phosphate 1–5 parts and 1–4% by volume of concentrated NaOH solution. The object is allowed to stand in the bath 5–30 min. at 30–40° c. It is then regularly rinsed vigorously and anodically oxidized in a bath containing $NaHSO_4$, 5–40; citric acid, 0·5–1; $Al_2(SO_4)_3$, 18; and H_2O, 0·5–1 parts per 100 parts water. The oxidation time clearly depends upon the passivity of the oxide layer but it is usually 5–20 min. To provide a highly reflecting surface (particularly for alloys), the object is then given 4–6 min. treatment in a 2N-H_2SO_4 and 0·1N-$Al_2(SO_4)_3$ bath at 80° c.

Confirmation of the structure of the electrically polished Al surface has now been given.[71] The surface was found to be identical with the internal composition of the metal, although several authors have recently claimed that it is covered with an oxide layer. Samples of 99·995% pure Al, polished in a $HClO_4$–Ac_2O bath, showed the diffraction pattern of monocrystalline Al. After 1 month's exposure to the air the pattern changed to indicate the formation of a thin oxide layer, which, by comparison with prepared Al layers was estimated to be 30–50A. thick. A mixture of H_3PO_4 and H_2CrO_4 in the polishing bath gave rise to an oxide layer immediately after polishing.

Finally, a good report on the 3-layer molten-salt cell for the refining of Al shot is now available.[72]

Antimony.—Comparatively little work has been carried out on the refining of Sb. This year there is a detailed report[83] of the refining of some Sb bullion in an electrolyte containing SbF_3 and H_2SO_4. The effects of electrolyte circulation and variation of the amount of Sb in the solution were studied. It was found that the current efficiency was about 99% and that the deposit stripped well. Most of the Cu, Sb, and Bi in the bullion went into the refined metal while more than 99% of the Au and Ag were recovered from slimes when the bullion contained S and As.

Iron.—A method for the electrolytic polishing of ferrous specimens which is superior for some purposes to mechanical polishing has been developed.[73] The polishing solution consists of 765 c.c. of acetic anhydride and 180 c.c. of well cooled 60% $HClO_4$, and 55 c.c. of H_2O. Specimens can be polished in 2 min. at 0·2 amp./cm.^{2} The electropolished specimens etch more rapidly than the mechanically polished specimens, and give more control between structural constituents. Electrolytic polishing is inferior to mechanical polishing in the preparation of graphitic Fe and steel, where the examination of the non-metallic inclusions is of primary importance.

The production of wire, rods, sheets and strips of stainless steel (Cr, 10–35%; C, 0·25–1·2%; the rest Fe) is achieved[74] most conveniently by another electropolishing process in which anodic connexion is established to the steel product and the latter moved through the bath of H_3PO_4–H_2SO_4 and diethylene glycol butyl ether.

The electrolytic production of Fe powder has also received some attention.[75] Of the two possible methods, grinding a coherent deposit is found to be cheaper than direct deposition on a cathode. The current efficiency is 95% and the power consumption only 1 kwh./lb. Fe.

The considerable hardness of electrodeposited Fe is known to be due, in part, to finely dispersed hydroxide. In a recent Swedish paper[76] a report is given of the deposition of brittle electrolytic Fe at 10–100 amp./dm^2., p_H 3–6·5, and at 20° and 50° C. from an electrolyte containing only 15 g./l. Fe as $FeCl_2$ and 100 g./l. NH_4Cl. The specimens showed microscopic traces of oxides after annealing in N_2 at 800° C. The author regards it as originally present, submicroscopically divided ferrous hydroxide. The latter is measured by the loss in weight undergone by a specimen upon annealing in H_2 at 950° C. Hydroxide content, micro-hardness, and internal stress decrease rapidly upon increase of electrolysis temperature, increase with c.d. and show a downward trend with increase of p_H.

Ferrous hydroxide is of more direct importance in the production of FeO pigments. The electrolytic production of $Fe(OH)_2$[77] is achieved by the electrolysis of aqueous NaCl with a Fe electrode. The anolyte (a $FeCl_2$ solution) is withdrawn and mixed with the catholyte (NaOH solution); the precipitate of $Fe(OH)_2$ is separated by filtration and the recovered NaCl solution returned to the cell.

Lead.—A great advantage is found in the electropolishing of this metal rather than the mechanical polishing, which takes an abnormally long time and is, further, dangerous because it may bring about changes in structure owing to the low recrystallization temperature. C. Chalin and I. Epelboim[82] have now found an economical method of carrying out the electropolishing. Two lead baths with Al cathodes, the bath composition being mainly acetic anhydride and perchloric acid are described, and excellent results are claimed.

Nickel.—A new, patented process for the electrolytic refining of nickel[78] involves the use of $Fe(OH)_3$. The Fe in the Ni anode is controlled to limit the Fe content of the electrolyte to 0·3–0·4%. This Fe, which is removed by aeration, carries with it adsorbed As, Pb and Cu. After filtration, freshly prepared $Fe(OH)_3$ is added to remove As, Pb and Cu, and the electrolyte is then refiltered and used for the electrolytic production of Ni. This process may be compared with one for producing modified Ni[79] in which a mixture of powdered Ni with one or more of the substances Li, Be, Na, Mg and Al is moulded to form an integral starting sheet, which is then immersed in a Ni electrolyte. A layer of the Ni is electrodeposited on the sheet, and this is then removed and heated to 400° F. At this temperature the modifying agent diffuses from the sheet to the electrodeposited metal.

The brightness of Ni deposits has not been studied to the same degree as some other metals. Largely negative results have been obtained by W. Smith, J. H. Keeler and H. J. Read[80] in a study of the correlation between brightness and preferred orientation of Ni deposits prepared from a Watts-type bath to which various brighteners were added. Brightness evaluations with the Hunter Multipurpose Reflectometer were different from those made by visual evaluations.

The anodic behaviour of nickel in alkaline solutions has been a subject of new interest in further Russian work. The current–voltage relations in alkaline solution show kinks at certain voltages, indicating the formation[81] of $Ni(OH)_2$ and its oxidation to Ni_2O_3. Similar inflexions are

shown on the charging curves. The mechanism of the overpotential associated with these changes is obscure.

Uranium.—The young and developing electrochemistry of U has been furthered with respect to electropolishing by P. A. Jacquet and R. Caillat.[84] Specimens, previously polished with 03 paper, were electrolysed in a mixture of 50–100 c.c. of 60–65% $HClO_4$ and 1000 c.c. of pure AcOH. Polishing took place in 5 min. at about 5–10 amp./dm^2. with a flat unoxidizable steel cathode. U is insoluble in the electrolyte in the absence of an applied field, but dissolves anodically to give U^{2+}. The polished surface remains bright in dry air but becomes yellowish, owing to oxidation, in moist air.

Condensers and dielectrics

Little work has been published in this field during the year. Filaments or sheets of TiO_2 or various titanates formed by extrusion have now been used as dielectrics for static condensers, the method of applying the film being described in detail.[85]

The alumina layer of the Al anodes of electrolytic condensers has been examined by means of *X*-ray analysis.[86] The 99·85% pure Al was subjected to 0–600 v. in a boric acid bath. The Al was removed from the oxide by solution in dry ether with HCl; the remaining oxide was examined with *X*-rays and the type of oxide formed was found to depend upon the applied voltage in the following way. 0·5–20 v.: α-$Al_2O_3.H_2O$, small, imperfect crystals; 50–200 v.: a mixture of α-$Al_2O_3.H_2O$ and γ-Al_2O_3; 580–600 v.: a mixture of γ- and γ'-Al_2O_3, layer and well developed crystals.

Cells

(i) *Primary*

A very useful review on the more recent industrial developments in the field of primary cells has been given by R. Huber.[87] The historical development of primary cells from the Leclanché cell is given and special attention is paid to the newest Hg and Mg microcells used in radio and in acoustic apparatus.

The alkaline primary battery has been the subject of a new and detailed investigation.[88] In batteries with a zinc anode and an electrolyte-regenerating material, e.g. lime, it is found that the effectiveness of the lime is diminished by the formation of a covering of calcium zincate which protects the lime from contact with the solution. An improvement is caused by the use of a mass of dry, powdered, hydrated lime, which is damped with water and forced through a coarse wire screen to form granules. When dried in hot air the granules become porous. The cell performance is also improved by using weaker caustic electrolyte, the best range being 2·5–5·5 N. In a further cell with Zn anode (amalgamated corrugated Zn foil is used)[89] the cathode depolarizer is an intimate mixture of 20–30% graphite with $AgMnO_4$. The anode is interleaved with a double layer of polystyrene fibre sheet. The electrolyte consists of a saturated solution of ZnO in 20–50% KOH.

An interesting new cell capable of withstanding a high drain is reported by E. Schaschl and H. J. McDonald.[90] The most successful version of the cell had a sodium anode, with iron as the inert electrode; the electrolyte

consisted of IBr_3 and $FeCl_2$ dissolved in SO_2. The open circuit voltage varied from 3·5 v. at room temperature to 2·7 v. at − 60° c. With high drain the corresponding voltages are 2·6 to 1·2 and the short circuited current 70–16 ma./cm^2.

The mechanism of corrosion in the Leclanché type of cells is found to be of two types.[91] The first is the hydrogen evolution type of corrosion in which the velocity of the reaction is controlled by the surface condition of the electrode owing to the effect of the latter on the over-potential at the metal. The second type is due to corrosion by high valency ions passing from the MnO_2 into the electrolyte. This reaction is controlled, in addition to obvious factors, by the diffusion of $HMnO_2$ ions from the depolarization electrodes to the Zn electrodes. In contrast with the first type of mechanism it is independent of the condition of the Zn.

(ii) *Secondary*

In a new version of the Pb accumulator,[92] the Pb is present as the fluorosilicate, the electrodes being graphite. When the cell is discharged, the PbO_2 trickles down the electrodes and becomes peptized by Pb ions. This is minimized by addition of polysulphonic acids. The accumulator is charged in 20 hr. by a current of 150 ma. and 2 v. The sulphation of ordinary accumulator plates[93] is accelerated by higher concentrations of H_2SO_4, high temperatures, lower specific gravity of the paste and higher PbO_2 content. The degree of moisture of the plates and the preliminary treatment with H_2O vapour do not affect the sulphation. The reconditioning of battery plates has been examined by A. L. Hindall[94] who subjected the negative plates of a Faure-type storage battery to a charge and discharge cycle in a solution of alkali metal sulphite and potassium tartrate to reduce the $PbSO_4$ and render the Sb soluble. The plates of the dismantled battery are first dried to oxidize Pb, immersed in 5% alkaline-earth hydroxide solution for 5 min., dried again and finally immersed in sulphite liquor. Absorption of the ingredients of the solution rejuvenates the expanders, and increases the life of the negative plate three times more than that of the positive plate. Sintered plates for Ni–Cd batteries[95] are prepared by sintering carbonyl Ni powder of low apparent density. Impregnation of the plaques is carried out with Ni or Cd salt solution, the heavy metal ions being precipitated in the pores of the plaque by cathodic polarization in alkaline hydroxide. Results are shown for a typical set of discharge curves with a 5-plate experimental cell for a range of the 20-hr. rate to the 3-min. rate. Other work on the Ni–Cd alkaline cell[96] includes a test of one developed by Accumulaten Fabric A-G., Hanover. The percentage reduction in capacity was the same as for the Pb–acid battery when the temperature was lowered to − 7° c. The capacity at − 20° c. was 10% greater than that of the Pb–acid cell.

The anodic behaviour of Pb–Ca alloys has been found to be inferior to the usual material containing Sb.[97] The capacity is decreased by Ni but increased by Sn, Sb and Mn. Growth of the plates is small for Pb–Ca, Pb and Pb–Ca–Ni but much greater for alloys containing Cu, Mn, Cd and Sb and worst for Bi and Sn.

Dry batteries have been the subject of a good general review by N. M.

Potter.[98] A new dry cell with a prolonged shelf life designed by S. Ruben[99] has a preferred solution of KOH (65%) and H_2O (35%), made by heating to 120° C. to dissolve the electrolyte. The cell assembly of steel strip is heated to 100° C. and immersed in the hot liquid electrolyte. Evacuation is used to improve impregnation of the space between the electrodes. At room temperature the electrolyte is a hard solid. In a further dry cell designed by the same author[100] the steel container lined with Zn encloses an anode composed of compressed amalgamated Zn powder containing Pb approximately 0·05 and Cd 0·002%. The spacer used is composed of 6 discs of 0·01-in. thick Dexter paper, and is housed in a polystyrene ring. The cathode depolarizer is a compressed pellet of red HgO 90% and micronized graphite 10%. A disc of plasticized polyvinyl alcohol is interposed between the spacer and the cathodes to prevent migration of deleterious particles, while a neoprene grommet ring insulates the bimetal (Zn–steel).

The shelf life of dry cells as a function of the gel strength of paste walls has been studied by W. J. Hamer[101] who finds that $ZnCl_2$ and NH_4Cl decrease the initial strength, whereas acetylene black and MnO_2 increase the initial strength of starch gels. The hydrolysis of the gels is increased by the presence of salts and MnO_2, which react with starch ; these reactions cannot be eliminated by using different varieties of starch or by the use of inhibitors. Cells were improved by using protein films on the surface of the Zn anode.

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References

[1] Heussner, C. E., Balden, A. R. and Morse, L. M., *Plating*, 1948, **35**, 554
[2] Senderoff, S., *Metal Finish.*, 1948, **46**, No. 8, 48
[3] Marlies, C. A., ibid., No. 10, 60
[4] Fischer, J., *Metalloberfläche*, 1947, **1**, 28
[5] Mehl, E., *Metal Ind., Lond.*, 1949, **74**, 268
[6] Graham, A. K., Pinkerton, H. L., Anderson, E. A. and Reinhard, C. E., *Plating*, 1949, **36**, 702
[7] Aluminium-Industrie A.-G., Swiss Pat. 221,732
[8] Johnson, A. F., U.S.P. 2,451,490
[9] Gadeau, R., *Bull. Soc. franç. Élect.*, 1947, **7**, 540
[10] Halls, E. E., *Industr. Finish. Gt. Brit.*, 1949, **2**, 30, 34
[11] Koizumi, K. *et al.*, Japan Pat. 177,313
[12] Salauze, J., *Bull. Soc. franç. Élect.*, 1949, **9**, 23
[13] Willson, K. S. and Ellis, D. G., U.S.P. 2,471,918
[14] Brown, H., U.S.P. 2,455,554
[15] Vuigner, E., *Bull. Soc. franç. Élect.*, 1944, **4**, 261
[16] Herbach, M. G. and Bowden, C. W., *Metal Progr.*, 1947, **51**, 257
[17] Bilfinger, R., *Arch. Metallk.*, 1948, **2**, 131
[18] Dale, J. J., Proceedings of 3rd International Electrodeposition Conference, 1947, 185
[19] Bilfinger, R., *Arch. Metallk.*, 1948, **2**, 27
[20] Ichizo, and Iitaka, *Bull. Inst. phys. chem. Research (Tokyo)*, 1943, **22**, 558
[21] Ibid., 1944, **23**, 107
[22] Ibid., 187
[23] Gebauer, K., *Arch. Metallk.*, 1948, **2**, 172
[24] Patrie, J., *Rev. Aluminium*, 1948, No. 149, 335
[25] Troescher, W. F., *Werkst. u. Betr.*, 1947, **80**, 67

[26] Dubpernell, G., U.S.P. 2,462,615
[27] Rüdorff, W., Hofmann, U., Rüdorff, G., Endell, J. and Ruess, G., *Z. anorg. Chem.*, 1948, **256**, 125
[28] Blue, R. D., Hunter, R. M., Neipert, M. P., U.S.P. 2,468,022
[29] Ksycki, M. J. and Yntema, L. F., *J. electrochem. Soc.*, 1949, **96**, 48
[30] Brenner, A. and Jennings, C. W., *Plating*, 1948, **35**, 1228
[31] Thon, N., Kelemen, D. and Yang, L., ibid., 1949, **36**, 362
[32] McQuire, R. C., U.S.P. 2,457,059
[33] Willson, K. S. and Du Rose, A. H., *Metal Finish.*, 1949, **47**, 55
[34] Jernstedt, G. W. and Ceresa, M., U.S.P. 2,470,775
[35] McCoy, E. H., U.S.P. 2,473,163
[36] Brenner, J. G. M., *Nature*, 1948, **162**, 1831
[37] Vozdvizhenskii, G. S., *Zhur. priklad. Khim.*, 1947, **20**, 1255
[38] Idem., ibid., 1171
[39] Liger, A. W., U.S.P. 2,474,092
[40] Loveland, T. A., U.S.P. 2,466,660
[41] Netherton, L. E. and Holt, M. L., *J. electrochem. Soc.*, 1949, **95**, 324
[42] Pirie, *Industr. Finish., Gt. Brit.*, 1948, **1**, 225
[43] Hesselberger, W. E., *Metal Ind., Lond.*, 1949, **74**, 66
[44] Gray, A. G., Gresham, W. F. and Loder, D. J., U.S.P. 2,461,507
[45] Seim, H. J. and Holt, M. L., *J. electrochem. Soc.*, 1949, **96**, 43
[46] Mansell, R., *Metal Finish.*, 1948, **46**, No. 12, 63
[47] Chester, D. E. and Reisinger, F., U.S.P. 2,461,809
[48] Bair, R. R., Benner, H. L. and Walker, J. F., U.S.P. 2,451,426
[49] Lowe, S. P., Long, G. W., Kent, G. H. and Downes, K. W., U.S.P. 2,471,965
[50] Kudryavtsev, N. T., Lipovetskaya, A. I. and Kharlamova, K. N., *Zhur. priklad. Khim.*, 1949, **22**, 377; *Chem. Abs.*, **43**, 6521, Sept. 10
[51] Gromov, B. V. and Negovorov Tsvetnye, B.A., *Metal*, 1947, **20**, No. 4, 26
[52] Anderson, A. E., Electrochem. Soc. and N. and H. Assoc. Corrosion Engrs., Symposium on Cathodic Protection, Dec. 1947 (Published 1949), 97
[53] Koizumi, K. *et al.*, Japan. Pat. 172,621, May 9, 1946
[54] Graham, K., Heiman, S. and Pinkerton, H. L., *Plating*, 1949, **36**, 47, 79
[55] Offermans, H. and Stackelberg, M. V., *Metalloberfläche*, 1947, **1**, 142
[56] Booe, M., U.S.P. 2,458,827
[57] Clark, W. E. and Holt, M. L., *J. electrochem. Soc.*, 1948, **94**, No. 5, 244
[58] Lietzke, H. M. and Holt, M. L., ibid., 252
[59] Schaefer, A. and Mohler, J., U.S.P. 2,461,350
[60] Miller, P. J. and Cuthbertson, J. W., *Metal Finish.*, 1949, **47**, 44
[61] Andrieux, J. L., *J. Four. élect.*, 1948, **57**, 26
[62] Jacquet, P. A., *Metal Finish.*, 1949, **47**, No. 5, 58; ibid., No. 6, 83
[63] Vozdvizhenskii, G. S., Dezider'ev, G. P. and Dmitriev, V. A., *Doklady Akad. Nauk U.S.S.R.*, 1949, **65**, 697
[64] Holt, M. C. N. and Ward, A. M., *J. Electropl. Depos. Soc.*, 1949, **24**, 33
[65] Nishida, Kozo, Japan. Pat. 154,087
[66] Barnabo, M., Ital. Pat. 422, 984
[67] Piatti, E., Swiss Pat. 240, 467
[68] Agma, A.-G., Swiss Pat. 242, 356
[69] Lucifer, M., S.A., Swiss Pat. 245,379
[70] Zeerleder, A. v. and Hübner, W., *Chimia*, 1949, **3**, 77
[71] Raether, H., *C.R. Acad. Sci., Paris*, 1948, **227**, 1247
[72] Helling, W. and Lay, H., *Erzbergbau und Metallhüttenw.*, 1949, **2**, 65
[73] Pow, J., *Metal Treat.*, 1949, **16**, 31
[74] Clingan, I. C., U.S.P. 2,461,036
[75] Wranglen, G., *Jernkontor. Ann.*, 1948, **132**, 501
[76] Johansson, E. H. E., Swed. Pat. 121,716
[77] Arend, A. G., *Paint Technol.*, 1946, **11**, 463
[78] Gronnüngsaeter, A. M. and Hommeren, B. G., U.S.P. 2,450,426
[79] Buck, M. P., Canad. Pat. 454,187
[80] Smith, W., Keeler, J. H. and Read, H. J., *Plating*, 1949, **36**, 355
[81] Volchkova, L. M., Antoneva, L. G. and Krasil'schikov, A. I., *Zhur. fiz. Khim.*, 1949, **23**, 714
[82] Chalin, C. and Epelboim, I., *Rev. gén. Élect.*, 1948, **57**, 254

[83] Schlain, D., Pratev, J. D. and Ravitz, S. F., *J. electrochem. Soc.*, 1949, **95**, No. 3, 145
[84] Jacquet, P. A. and Caillat, R., *C.R. Acad. Sci., Paris*, 1949, **228**, 1224
[85] Pridham, E. S., U.S.P. 2,448,952
[86] Brandenberger, E. and Häfeli, R., *Helv. chim. Acta*, 1948, **31**, 1168
[87] Huber, R., *Mitt. chem. Forsch.-Inst. Ind. österr.*, 1948, **2**, 124
[88] Le Roy, Dunham, S. and Jegge, E. O., U.S.P. 2,450,472
[89] Ruben, S., U.S.P. 2,462,998
[90] Schaschl, E. and McDonald, H. J., *J. electrochem. Soc.*, 1948, **94**, 299
[91] Drotschmann, C., *Metall*, 1949, **3**, 84
[92] Haayman, P. W., Romeyn, F. C., Verwey, E. J. W., Dutch Pat. 61,306
[93] Skalozubov, M. F., *Zhur. priklad. Khim.*, 1949, **22**, 307
[94] Hindell, A. L., U.S.P. 2,451,087
[95] Fleisher, A., *J. electrochem. Soc.*, 1948, **94**, 289
[96] Chu, G. D., National Research Council of Canada, Elect. Engng. Radio Branch, Rept. No. ERB–172, 1947
[97] Hoehne, *Arch. Metallk.*, 1948, **2**, 311
[98] Potter, N. M., *J. Brit. Inst. Radio Engrs.* (*N.S.*), 1949, **9**, No. 2, 61
[99] Ruben, S., U.S.P. 2,463,565
[100] Ruben, S., U.S.P. 2,458,878
[101] Harner, J., *J. Res. nat. Bur. Stand.*, 1948, **40**, 251

ACIDS, ALKALIS AND SALTS

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NATIONAL economic limitations and the increasing world demand for key raw materials in the chemical industry as a whole are strikingly reflected in the effort put into the development of recovery processes and in attempts to use alternative sources of supply. Thus during the year under review there have been many references to recovery processes for sulphur, for hydrochloric acid and for hydrofluoric acid. Suggestions have also been made to obtain potassium from cement and flue dusts. The oil and petroleum companies in particular are showing interest in the reclaiming of the acids used in that industry.

In the chemical fertilizer industry there have been more references than in the previous year to ammonium sulphate. In the phosphate field there is further evidence of interest in recovery processes ; low-grade sources of phosphate-containing materials have been enriched by treatment and also other raw materials for the chemical industry have been economically recovered from phosphate rocks.

Of the halogen compounds, fluorine has received by far the greatest attention and a number of reviews has been published on the commercial exploitation of the element and its compounds.

Carbon disulphide is another compound, which during the year, has received considerable attention.

Nitrogen compounds

The production and consumption of anhydrous ammonia in the U.S.A. is reviewed by J. R. Skeen.[1] This product is now manufactured by a modified Haber process using a promoted iron catalyst and by-product hydrogen, the major difference from the original process being the source of hydrogen. It is estimated that current American production is nearly 1·5 million tons. In hydrogen and nitrogen mixtures for ammonia synthesis, according to an American Patent by J. H. Shapleigh,[2] the nitric oxide responsible for corrosion is removed by reduction with hydrogen in the presence of a catalyst. Thus nitrogen-rich gases containing 80–100 p.p.m. nitric oxide, when passed over nickel catalyst in the presence of hydrogen at the rate of 400 cu. ft. gas/cu. ft. catalyst, give a product containing less than 1 p.p.m. of nitric oxide. In another patent[3] dealing with the production of ammonia from hydrogen and nitrogen, these two gases are passed over a mixture of 75% magnesium and 25% nickel at 270°–300° C. The production of synthetic ammonia from coke oven gas has been reviewed.[4] The coke oven gas is washed with water and caustic soda to remove carbon dioxide and cooled to − 180° C. to remove hydrocarbons. It is then fractionated with liquid nitrogen to condense out the carbon monoxide and give a final mixture containing

92% hydrogen and 8% nitrogen which is then adjusted for ammonia synthesis. It is compressed to 250 atmospheres and synthesis is effected at 250° C. on a suitable catalyst.

There have been a few more references to ammonium sulphate during the year than in the previous year. According to R. L. Taylor[5] ammonium sulphate is being made from ammonia and sulphuric acid in a war-time alumina plant employing normal methods for control of crystal size and shape. The Fuel Refining Corporation[6] have patented a method for the producton of large crystals of ammonium sulphate by passing coke oven gas into 5·5% sulphuric acid. The gas is introduced through the vertical cracker pipe and the liquor directly below it is circulated upwards by motor-driven vanes. Make-up acid is sprayed against the inside of the pipe thus avoiding deposition of crystals. Another method for the manufacture of ammonium sulphate, this time from spent pickling liquor and coke-works ammonia, has been patented by C. B. Francis.[7] The crude ammonia is added to the spent acid until a p_H of 2 is reached. The rate of addition of ammonia is then adjusted so that the p_H is maintained at 4–5, the temperature being raised to 70°–80° C. and the solution is aerated. After all the iron has been precipitated, further ammonia addition precipitates aluminium at p_H 7 and manganese at p_H 11. After filtration the ammonium sulphate is recovered from the filtrate by the usual methods. Yet another method for ammonium sulphate production has been described in an I.C.I. Ltd. patent.[8] In this method anhydrite is treated with ammonia and carbon dioxide to give calcium carbonate, which is filtered off with unchanged anhydrite, while the ammonium sulphate is crystallized from the mother-liquor.

The recovery of ammonium thiosulphate and thiocyanate from spent gas washing solution has been described in an American patent of the Koppers Co. Inc.[9] Alcohol is added to the liquor after evaporation to give an aqueous phase which is treated with more alcohol to precipitate the pure thiocyanate, and an alcohol phase which is similarly treated to precipitate the thiosulphate. Normal ammonium fluoride can be converted to ammonium bifluoride according to F. M. McClenahan[10] by heating the aqueous solution of the fluoride to about 100° C. in order to expel water and then to 115° C. to expel ammonia. Finally it is heated to 125° C. until almost all the fluoride is converted to the bifluoride.

The distribution of impurities in the crystallization of ammonium and potassium alums has been studied by D. Schain, J. D. Prater and S. F. Ravitz,[11] who showed a correlation between the ionic radii of the impurities and the displaced ion of the alum lattice. The distribution of the impurities followed the Doerner–Hoskins equation.

An excellent account of the chemistry of hydrazine is given by L. F. Audrieth and D. H. Mohr.[12] Physical and chemical properties are given in relation to other nitrogen–hydrogen compounds. A description is given of its production by modification of the Raschig process wherein ammonia or urea is oxidized by sodium hypochlorite at low temperature and with excess ammonia. Rapid heating is then necessary to effect the formation of hydrazine from chloroamine and ammonia. A negative catalyst, such as glue or gelatin, inhibits the catalytic effect of copper to decompose the hydrazine. Anhydrous hydrazine is made by the action

of potassium or sodium hydroxide on the solution, or by treating the hydrazine salts with liquid ammonia.

Nitrates.—The action of nitric acid on various construction materials has been summarized by A. W. Spitz *et al.*[13] Durimet shows excellent resistance at all concentrations. Experiments to obtain nitric oxide from air have been described by N. Gilbert and F. Daniels.[14] The air was heated to above 2100° C. in a packed furnace and the combustion gases were rapidly chilled. About 1·75% of the air was converted into nitric oxide. The authors give the equilibrium concentrations of nitric oxide in air, the reaction rates for formation and decomposition of the nitric oxide and the experimental yields. The solubility of nitric oxide in nitrose has been determined by A. N. Tseitlin.[15] The amount of nitric acid absorbed is proportional to the concentration of nitrogen trioxide in the nitrose and increases with decreasing specific gravity of the nitrose.

According to a patent by the Union Chim. Belg. S.A.,[16] ammonium nitrate can be produced by distilling ammoniacal liquor from coke manufacture and introducing the vapours into a saturator containing aqueous ammonium nitrate and nitric acid at a temperature below the condensation temperature of the water vapour. Nitric acid is then introduced at such a rate that there is never more than a slight excess of it. According to a patent assigned to the Solvay Process Co.,[17] pebbled ammonium nitrate is produced by heating a mixture of ammonium nitrate, powdered dolomite and water at 110°–133° C. in a counter-current air stream. The water content, 0·3–4·0%, depends upon the temperature of the counter-current air stream. G. S. Scott and R. L. Grant[18] have given a long review with 115 references of the fire and explosion hazards of ammonium nitrate. Although ammonium nitrate does not decompose spontaneously at ordinary temperatures, it may react or decompose in the presence of reducing agents or organic matter. The authors review the conditions of detonation in some detail. Lonza Elektrizitätswerke and Chem. Fabr. A.-G.[19] have patented a method for the manufacture of granular calcium nitrate with a low water content by slowly evaporating aqueous calcium nitrate to a concentration of 92%. This melt is then sprayed in centrifugal machines to break it up and allow it to solidify.

The American Cyanamid Co.[20] have patented a method for the preparation of cyanamide by reacting calcium cyanamide slurry with carbon dioxide and forcing the mixture through closely fitting blades. Cyanamide is obtained from the resulting slurry by filtering off the calcium carbonate.

E. I. du Pont de Nemours & Co.[21] have patented a catalyst for hydrogen cyanide production, which consists of a refractory coated with platinum. Before passing over this catalyst, the pre-heated hydrogen and cyanogen are treated with a non-porous refractory free from platinum. A method for the stabilization of hydrogen cyanide by the addition of 0·25–3·0% of cobalt oxalate, with or without nickel oxalate, has been patented by A. Sporzyanski.[22]

Phosphates

The production and consumption of phosphates has been reviewed[23,24] while J. Sorel[25] has decribed the industrial preparation of phosphorus and its compounds.

According to F. R. Hunter,[26] it is economically possible to recover the small amounts of heavy minerals, including ilmenite, present in the pebble phosphate deposits of Florida. The Southern Phosphate Corporation[27] has patented a method for separating quartz sand from phosphate rock by floating it in the presence of a cationic agent and a petroleum oil. Laboratory-scale flotation of brown rock phosphate has been reported by J. E. Davenport and J. F. Hauman,[28] who have investigated methods of improving low-grade phosphate sand. The final process comprises grinding the ore, scouring, de-sliming, conditioning at p_H 8–9 and then effecting a two-stage fractional flotation using kerosene and a vegetable oil distillate as collector. More than 90% of phosphate containing 27% P_2O_5 can be recovered. The de-fluorination of phosphate rock is described in a patent by the Coronet Phosphate Co.[29] A mixture of phosphate rock and silica is calcined in steam in a rotary kiln at 1427–1649° c. for about 5–20 min., the pressure being slightly above atmospheric. The resultant product is cooled qu:ckly and ground to the desired size.

The development of the phosphorus industry in the United States has been reviewed by J. R. Skeen.[30] The electric furnaces now in general use operate the two-stage process, recovering the element and then converting it to the pentoxide and phosphoric acid. The production of red phosphorus from yellow phosphorus, by boiling the latter until 50% is converted, is described in a patent issued to the Tennessee Valley Authority.[31] The red phosphorus is separated from the fluid mixture by sedimentation followed by distillation. Final traces of yellow phosphorus are removed by solvent extraction. According to M. S. Silverstein[32] the stability of red phosphorus can be improved by the addition of mannitol, dextrose or phloroglucinol.

The new phosphorus combustion system of the Tennessee Valley Authority has been described by L. H. Almond and H. K. Steinbiss.[33] This makes use of a graphite combustion-chamber where the phosphorus is burned in an improved burner nozzle. The acid gases are cooled in a tubular graphite water-cooled heat-exchanger. The instrumentation and control system are briefly described. A blast furnace process for the production of phosphoric acid on an experimental scale has been described by T. P. Hignett.[34] A considerable number of data on the size of coke and phosphate rock, furnace temperature, dust content and furnace behaviour have thus been collected and tabulated. Arrangements to effect fuel economy and the effect of various fillings have been studied in detail. In a later article the same author[35] further investigates the production of phosphoric acid and describes conditions for obtaining the phosphorus pentoxide with 100% yield. The Southern Phosphate Corporation[36] have patented a wet process for phosphoric acid manufacture in which phosphate rock is heated with aqueous phosphoric acid to give a phosphate complex which is digested with a mixture of sulphuric and phosphoric acids to give 70–75% phosphoric acid and readily filterable calcium sulphate. According to another patent by the same company,[37] pure phosphoric acid is obtained by heating phosphate rock with phosphorus pentoxide and mixing it with phosphoric acid, agitating and diluting to 75% phosphoric acid, filtering and mixing the filtrate with sulphuric acid to precipitate the calcium sulphate which is removed.

The filtrate contains ortho- and meta-phosphoric acids which are subsequently recovered in the pure form. Another patent,[38] again by the same company, describes the production of crude phosphoric acid; in this process calcium phosphate is heated with concentrated phosphoric acid to form a soluble calcium phosphate and the calcium is removed by precipitation with sulphuric acid. The Davison Chemical Corporation[39] has patented a method wherein superphosphate granules are leached with 28·5% sulphuric acid without mechanical mixing or heating to produce, without evaporation, a phosphoric acid of 55–70% strength which is free from calcium sulphate. In another patented method[40] for the production of phosphoric acid by the wet process, natural calcium phosphates are decomposed with nitric acid to form calcium nitrate and phosphoric acid.

R. N. Bell[41] has determined the composition of strong phosphoric acids for mixtures between $P_2O_5.H_2O$ and $P_2O_5.3H_2O$. The three acids identified in addition to H_3PO_4 were $H_4P_2O_7$, $H_5P_3O_{10}$ and $(HPO_3)_6$. The sodium salts of the three acids were prepared and identified.

Turning to the production of superphosphates, J. A. Lee[42] has described a new plant at Charleston for the production of sulphuric acid from sulphur and of superphosphates from phosphate pebbles and concentrates. Provision is made for removing the hydrofluoric acid generated during the process. R. Enterprise and J. Moritz[43] have patented an apparatus for eliminating the friction, which occurs between the superphosphate and the working parts, in order to prevent the formation of hard lumps of superphosphate.

The production of trisodium phosphate dodecahydrate is described in a patent issued to the Monsanto Chemical Co.[44] In this the titration ratio of aqueous trisodium phosphate is adjusted to 1·05–1·3, sodium silicate is added to give 0·5–2% of SiO_2 in the solution and the solution is then cooled to give crystals with a pre-determined bulk density. In another patent issued to the Monsanto Chemical Co.[45] sodium phosphates are produced continuously by treating sodium carbonate with the mother-liquor from disodium hydrogen phosphate crystallization to form a slurry which is treated at 90° c. with phosphoric acid in a quantity insufficient for neutralization. After being kept at 85°–87° c. until saturated, the mixture is passed to a continuous crystallizer where the disodium phosphate is separated, the mother liquor being filtered, heated and recycled. E. P. Partridge and C. R. Texter[46] have briefly reviewed the development and uses of Calgon (sodium metaphosphate). Albright and Wilson Ltd.[47] have patented a process for the manufacture of a free-flowing sodium polyphosphate hexahydrate ($Na_5P_3O_{10}.6H_2O$) by incorporating the stoichiometric amount of water into the polyphosphate while agitating.

According to Hall Laboratories Incorporated,[48] alkali phosphate glazes can be stabilized by adding compounds such as amines or alkali compounds so that the aqueous solution has a p_H of less than 8·3. The removal of fluorine from calcium phosphate is described in a patent issued to the International Minerals and Chemical Corporation.[49] The calcium phosphate free from fluorine is produced from apatite by grinding, adding 35% of phosphoric acid, mixing, curing, re-grinding and calcining in a rotary counter-current kiln at 1200° c. for $1\frac{1}{2}$ hr. A product with low fluorine content suitable for animal feeding stuffs can be made by calcining apatite, grinding, adding calcium oxide or carbonate and 20%

water and calcining at 1100° C. The Ozark-Mahoning Co.[50] have patented a process for preparing fluorophosphoric acid by treating phosphoric acid with undiluted phosphoryl fluoride at 70°–80° C. The reactions are carried out at 80° C. in stainless steel or pyrex glass vessels with reaction times of 4–9 hr.

Sulphur compounds

The process for the recovery of sulphur from sulphur flotation concentrates is described in a patent specification by A. B. Menefee and H. H. Greger.[51] The raw material is heated to liquefy the sulphur and the molten mass is treated with a reagent which is insoluble in the molten sulphur and which therefore wets the gangue. In another patent[52] it is claimed that elementary sulphur can be recovered from sulphurous gases containing hydrogen sulphide by passing the gases over a catalyst at 870°–980° C. in the presence of oxygen. A method for recovering sulphur from smelter gases containing sulphur dioxide has been patented by the American Smelting and Refining Co.[53]; the gases containing sulphur dioxide are treated at 1200° C. with hydrocarbon fuel and the mixture is passed at 425°–450° C. over a bauxite catalyst and thence, after cooling, to a sulphur precipitator. The exit gases from this go through a second catalyst chamber so that all the sulphur compounds are recovered as sulphur. The same company has another patent[54] for sulphur recovery where the gas is reduced with natural gas at temperatures above 1200° C. After cooling, the gas stream is passed into a catalyst chamber to convert the sulphur compounds to sulphur. Further cooling follows, the gas then passing to a sulphur precipitating unit. The gases can be heated again and the operations repeated. According to a patent by the Southern Acid and Sulphur Co.,[55] sulphur can be recovered from gases containing hydrogen sulphide by passing them, with oxygen, over a non-catalytic ceramic at 700°–800° C. followed by cooling to 155°–165° C. to give liquid sulphur. A method for the solvent extraction of sulphur from materials such as spent oxide containing free sulphur, has been patented by W. C. Holmes & Co., Ltd.,[56] the spent oxide, e.g. from coal gas purification, is extracted with aromatic hydrocarbons such as toluene or xylene. The design of the apparatus is claimed.

When sulphur is discoloured with organic matter, it may be decolorized, according to A. B. Menefee and H. H. Greger,[57] by adding an inert absorbent material to the molten mass. This is followed by treatment with 1·26–4% of 98% sulphuric acid; after stirring and filtration a decolorized product is obtained. The Lederle Laboratories Inc.[58] have patented a soluble sulphur ointment in which sulphur and calcium oxide are heated together in the presence of a polyhydric alcohol. R. C. Ulmer and J. F. Churchill[59] have described briefly the use of sulphur burners for the production of SO_2 for controlling the p_H value of alkaline waters. The process is simple and efficient and cheaper than when sulphuric acid is used.

The extraction of a gaseous mixture of sulphur dioxide and a low-boiling hydrocarbon with a mixture of a liquid organic sulphone and a liquid paraffin is claimed by the Dow Chemical Co.[60]; the sulphur dioxide is absorbed in the sulphone, removed and separated, leaving the hydrocarbon

in the paraffin. In another patent by the same company,[61] the sulphur dioxide is extracted from mixtures by the use of a liquid hydrothiophenoxide. W. S. Reid[62] has discussed sintering machine practice and illustrated with suitable diagrams various methods of concentrating sulphur dioxide by its re-circulation. A method of preparing liquid sulphur dioxide from ore sintering and recent developments are also described. N. W. Coster, L. M. Johnson and R. I. Theime[63] have described a process for recovering sulphur dioxide from sulphite gases. The sulphur dioxide is absorbed by counter-current absorption in a water tower and stack. 40 lb./ton of sulphur are recovered from bleached sulphite pulp. In the manufacture of sulphur dioxide, by the vaporization of sulphur and combustion of the vapour, the dirt and ash, according to a patent issued to E. I. du Pont de Nemours & Co.[64] can be separated from the molten sulphur by settling it and returning the settled sulphur to the volatilization zone. O. Wurz and E. Wurz[65] describe the use of copper pyrites for producing sulphur dioxide for use in a pulp mill. They emphasize the necessity for careful operation as sulphur trioxide tends to be formed.

Sulphuric acid can be recovered from dilute spent alkylation acid by concentrating to 90% sulphuric acid and passing through a closed chamber in two separate streams in vapour contact with each other.[66] One stream is at a low temperature and the other just below the boiling point of the acid. As the pressure in the chamber is less than the vapour pressure of the hot acid the water is transferred from the hot to the cold acid. In another process[67] for the recovery of sulphuric acid from alkylation sludges, the spent acid is diluted to 50%, the hydrocarbons removed and the acid re-concentrated; the sulphur dioxide produced is converted to the trioxide which is absorbed in the concentrated acid. Alkylation spent acid can also be used for the preparation of sulphur dioxide by distillation of the acid in a Mannheim furnace followed by high-temperature (810° c.) burning of the gases. This process is described in a patent issued to the Stauffer Chemical Co.[68] In another process[69] for the recovery of sulphuric acid from acid sludge, the latter is mixed with four volumes of kerosene, settled and hydrolysed with 30% sulphuric acid to give an increased recovery of sulphuric acid of from 83–94%. The Standard Oil Development Co.[70] have patented another method of recovery; in this method nitric acid is added to the dilute sulphuric acid containing carbonaceous matter; the mixture is heated and concentrated to 80–81%, which causes the distillation of a constant-boiling mixture of nitric acid and water. The residue is heated to remove all the oxides of nitrogen and it is concentrated to give an 88–92% sulphuric acid. Still another process by the General Electric Co.[71] claims the recovery of sulphuric acid by dispersing the waste acid in the presence of a heating gas containing free oxygen. The mixture is heated to about 480°–760° c. to form sulphur trioxide and water which are recombined to form sulphuric acid. In another patent by the General Electric Co.[72] the waste sulphuric acid is dispersed and treated with hot combustion gas in the presence of a reducing agent, when about 80% of the sulphuric acid is converted into sulphur dioxide. The above methods are concerned with the recovery of sulphuric acid from waste acids containing organic impurities, but in a

method patented by the National Lead Co.,[73] the waste acid comes from ilmenite treatment in the manufacture of titanium oxide. This waste liquor is treated with finely ground iron sulphide and the hydrogen sulphide evolved is collected and oxidized to sulphur for the manufacture of sulphuric acid. The other constituent of the waste acid, namely ferrous sulphate, is mixed with calcium hydrosulphide to give a mixture of calcium sulphate and iron sulphide which is heated with coke to convert the calcium sulphate into the sulphide. The product is then treated in water with hydrogen sulphide to regenerate the hydrosulphide for re-use. The insoluble iron sulphide is used partly to treat more waste acid and the other part roasted to produce sulphur dioxide.

According to M. S. Gelfman[74] better absorption of sulphur trioxide is obtained with a nitric acid–sulphuric acid–sulphur trioxide mixture than with a nitric acid–sulphuric acid mixture or with 98% sulphuric acid.

Recent U.S. production and consumption figures for sulphuric acid have been discussed, and the latest methods of production are given at some length by M. L. Kastens and J. C. Hutchinson.[75] A feature of the plant is the compactness of the sulphur burner gas filter, convertor and absorption tower unit giving high yields for a minimum of space. A major innovation in this plant is that the entire plant except the control room, blower and water-feed pumps, is exposed to the weather. Lead vessels and flues have been eliminated by pre-drying in the combustion air. The gas from the sulphur burners contains 9% of sulphur dioxide which is cooled to 405°–415° c. in a waste-heat boiler and filtered before entering the converters. After 70% has been converted in the first converter the gas passes to a second waste-heat boiler and is re-introduced to the second converter. The final conversion to sulphur trioxide is not less than 97·5%. For oleum production the gases are cooled to 150° c. and the sulphur trioxide absorbed in 20% oleum. The final exhaust gases contain only a trace of sulphur trioxide. The 98% sulphuric acid at temperatures of less than 50° c. is handled in cast iron pipes while the oleum is handled in steel pipes. The present trends of this process are towards larger sulphur-burning units giving capacities for single units of up to 500 tons of acid a day. The new open-air plant at Hamilton, Ontario, for the manufacture of sulphuric acid by the contact process has been described by H. L. Fanshaw.[76] According to a patent by I.C.I. Ltd.,[77] a new process for the production of sulphuric acid or oleum consists of burning molten sulphur in air at 350° c. and cooling the exit gas in a waste heat boiler to give a gas at 100° c. containing about 14% of sulphur dioxide. This gas goes to a contact convertor and after conversion the gas, now containing sulphur trioxide, is cooled by mixing with air in order to give a maximum conversion temperature in the convertor. H. C. Millett[78] has described in some detail the construction and operation of the plant at Flixborough for the manufacture of 110 tons/day of contact sulphuric acid from arsenical pyrites. The General Chemical Co.[79] proposes to produce oleum by passing a gas containing 8·6% sulphur trioxide through a tower containing 30% oleum. This gives an enriched gas which can then be converted to 60% oleum. The corrosion of construction materials by sulphuric acid has been reviewed; W. A. Luce, J. A. McHard, L. R. Scribner and E. P. Mampe[80] have dealt with the

action of sulphuric acid on high-silicon irons, silicones, tantalum and Haveg plastic, and F. E. Herstein, K. H. Roll and W. A. Luce[81] have given brief notes on the use of chemical stoneware, lead, Chlorimets, protective coatings, nickel and nickel alloys for the construction of plant for handling sulphuric acid. The corrosion problems occurring on a contact sulphuric acid plant have been reviewed by M. G. Fontana,[82] who concluded that corrosion due to acid mist can be eliminated by drying the air feed to the sulphur burners, while the corrosion of steel or cast iron pipes in the sulphur melting pits can be avoided by replacement with aluminium tubes. The cast iron blowers should be replaced by a cast iron containing 2% of copper, whereas steel is preferred to cast iron in the oleum coolers.

In reviewing the development of chamber acid plants, A. M. Fairlie[83] considers that the design and construction of the conical Mills–Packard chamber has now been further improved with a consequent saving in lead and increase in corrosion resistance. The improved plant capacity is 2·6–3·5 cu. ft. of chamber space per lb. of sulphur per day, and these figures can be further reduced in practice. W. H. Dyson[84] considers that a low volume/area ratio and a system of heat removal by internal spraying must be incorporated for successful Packard plant operation.

The Krebs Co.[85] have patented a method for the manufacture of sulphuric acid and common salt by treating solid sodium sulphate with gaseous hydrochloric acid to give sodium chloride and crude sulphuric acid. L. M. Clark and H. M. Spittle[86] have investigated the reaction between hydrogen and pyrites at 625°–650° c. and, with a space velocity of 40–50 volumes of hydrogen per volume of pyrites, they obtained a good yield of hydrogen sulphide. The same authors also found that the reaction of iron sulphide with steam or sulphur dioxide to produce hydrogen sulphide or sulphur is not practicable, but that the exothermic combustion of iron sulphide yields sulphur dioxide in concentrations suitable for the manufacture of sulphuric acid.

A number of processes have been put forward for the manufacture of carbon disulphide which is now being produced in the U.S.A. at the rate of 178,000 tons/yr.,[87] the rayon industry being the leading consumers. The New Jersey Zinc Co.[88] has claimed a process for the manufacture of carbon disulphide from carbon and sulphur in two stages, the first being the formation of carbonyl sulphide at 600°–900° c. and the second a conversion of this to the carbon disulphide at 1100°–1300° c. The reaction is carried out in a vertical muffle retort and yields of 70–90% on the sulphur are obtained. In a patent by A. D. Little Inc.[89] for carbon disulphide preparation, molten sulphur is fed to a carbon-containing heated tower. The sulphur is obtained by compounding sulphur with halogens, sulphur halides or organic sulphides to give a liquid sulphur phase of low viscosity. The Great Lakes Carbon Corporation[90] has patented a method for carbon disulphide manufacture by treating hydrocarbon residues at 150°–260° c. in the liquid phase with sulphur. The mixture is calcined to eliminate the hydrogen as hydrogen sulphide and to give a reactive carbon which can then be treated with sulphur vapour at 595–980° c. to give the required carbon disulphide. The Standard Oil Development Co.[91] have proposed a fluidized–solid process for producing carbon disulphide, by pre-heating finely ground coke with a deficient

supply of air and passing the fluidized mixture at 760°–870° C. into the upper part of a reaction vessel. The mixture descends a central pipe and comes into contact with ascending vaporized sulphur. The resultant carbon disulphide is freed from dust and condensed. Another patent[92] by the same company also describes the use of fluidized coke which is fed, together with sulphur vapour, into a reaction chamber at 760°–870° C. and the carbon disulphide thus formed is separated. The Stauffer Chemical Co.[93] have claimed a method for the purification of crude carbon disulphide by scrubbing it with liquid carbon disulphide in a dephlegmating column to remove sulphur and solid impurities; carbon disulphide vapour is then obtained free from hydrogen sulphide and can be condensed.

In a patented method[94] for the manufacture of thionyl chloride ($SOCl_2$), sulphur monochloride is heated below its boiling point and chlorine and additional sulphur chloride (S_2Cl_2) are added to form sulphur dichloride (SCl_2) which is vaporized, mixed with sulphur dioxide and chlorine, and passed over hot activated carbon at a reaction temperature of 175°–200° C. The thionyl chloride and sulphur chloride are condensed and distilled with excess sulphur; pure thionyl chloride is recovered as the distillate. The residue of sulphur chloride and sulphur is chlorinated and re-cycled. In another patented process[95] for the manufacture of the same compound, a mixture of carbon tetrachloride, sulphur dioxide and aluminium chloride is autoclaved at 150° C. for 8 hr. at 40 atm. pressure. After removal of a small amount of carbonyl chloride by condensation the resultant dark liquid is distilled to produce thionyl chloride. An American Cyanamid patented process,[96] for the production of sulphuryl chloride (SO_2Cl_2), consists of heating sodium chlorosulphonate to 400° C. to generate chlorine and sulphur dioxide; these are passed over granular activated carbon in a water-jacketed chamber and the resulting liquid sulphuryl chloride is condensed. The same company have also patented a process[97] for the production of pyrosulphuryl chloride; sulphur monochloride is added to liquid sulphur dioxide in a closed tank and the mixture heated for one hour at 75° C. and 165 lb./sq. in. pressure. The released gases are scrubbed in a tower to recover the sulphur dioxide and the residual pyrosulphuryl chloride which is formed may be distilled to remove sulphur monochloride and dissolved gases.

The harmful effect of selenium in the cyanide leaching of gold ore has been discussed by I. N. Plaksin, N. A. Suvoroskaya and A. V. Astafeva.[98] It is possible to extract selenium from the ore by treating it with calcium hypochlorite to produce selenic acid from which the selenium is precipitated by sulphur dioxide or metallic iron. According to Canadian Copper Refiners Ltd.,[99] when selenium dioxide is treated in the vapour phase with gaseous ammonia, pure elementary selenium can be condensed at 215°–260° C. Standard Telephones and Cables Ltd.[100] claim the manufacture of selenium elements by depositing the selenium on a base plate in an atmosphere of carbon dioxide and steam. According to the International Telephone and Radio Manufacturing Corporation[101] a smooth selenium surface can be obtained when a suspension of selenium powder in methanol is sprayed on to a base plate followed by evaporation of the vehicle. Selenium dioxide free from elementary selenium is made by

oxidizing selenium in the vapour phase with air, or oxygen, in the presence of copper oxide or chromium oxide or magnesium oxide as catalyst, according to a patent by the Canadian Copper Refiners Ltd.[102]

Halogen compounds

Fluorine and fluorine compounds.—A number of reviews on the subject indicate that still further progress has been made in the commercial exploitation of the element fluorine and its compounds.[103] The production and consumption of calcium fluoride in the U.S.A. in relation to fluorine compounds in industry has been reviewed by N. T. Hamrick and W. H. Voskuil.[104] The highest-grade fluorspar containing not less than 98% calcium fluoride is used for the manufacture of hydrofluoric acid and its derivatives. The second grade, 95–98%, is used in ceramics for vitreous enamels and opal glass, and the low-grade material, but not less than 85% calcium fluoride, is used in metallurgy as a flux. It is pointed out that the superphosphate industry, using rock phosphate containing about 3% fluorine, should in the future provide a substantial quantity of fluorine which can be recovered as hydrofluosilicic acid. G. C. Finer and F. H. Reed[105] have continued their review dealing especially with the industrial preparation and uses of fluorine chemicals. I.C.I. Ltd.[106] have patented the purification of fluorspar containing calcium carbonate, silica and galena by leaching it with 5–10% hydrofluoric acid and roasting in air or oxygen at 500°–1000° c. The enriched fluorspar is then suitable for the production of hydrofluoric acid. A U.S. Bureau of Mines report[107] has described the examination of fluorite ores by ore-dressing methods. A. J. P. Wilson[108] has reviewed present and future trends in the use of fluorspar and fluorine compounds, particularly in the U.S.A. whose fluorspar production of 343,700 short tons in 1947 was about one-third of the world's total. Here again phosphate rock is mentioned as one of the largest future sources of fluorine.

The industrial production of anhydrous hydrofluoric acid has been described[109] together with details of constructional materials for the different parts of the plant. There have been several references to the recovery of fluorine compounds from hydrocarbons. The Phillips Petroleum Co.[110] have patented a process for recovering hydrofluoric acid substantially anhydrous from azeotropic hydrogen fluoride–water mixtures by fractionation. The Standard Oil Co.[111,112] propose to recover fluorides (hydrogen or boron fluoride) from hydrocarbons containing them, by treatment with a diaryl ketone such as benzophenone and heating the resultant product to regenerate the absorbed fluorine compound. The Standard Oil Co.[113] also have another patent for the recovery of volatile fluorides from a hydrocarbon gas mixture by scrubbing with a counter-current stream of dihydroxyfluoboric acid and then heating the solution in a desorber. The Phillips Petroleum Co.[114] propose to obtain anhydrous hydrogen fluoride from aqueous solutions by adding a liquid hydrocarbon and an amine; the amine hydrofluoride is thus extracted in the hydrocarbon and then stripped to recover the anhydrous hydrogen fluoride. Another patent by the same company,[115] describes how low-boiling paraffin hydrocarbon containing hydrogen fluoride is passed as vapour counter-current to a liquid containing an organic base

such as an alkyl or aryl amine to extract the hydrogen fluoride which is then recovered in anhydrous form. The Universal Oil Products Co.[116] have patented the recovery of hydrogen fluoride by extraction of the hydrogen fluoride catalyst with aqueous hydrogen fluoride. The extract is then fractionated to obtain the anhydrous product. The Monsanto Chemical Co.[117] have claimed a process for recovering fluorine compounds from phosphate sinter gases by scrubbing them with dilute hydrofluosilicic acid saturated with an alkali metal silicofluoride. An alkali carbonate is then added to precipitate the silicofluoride from the scrubbing liquor.

Chlorine.—A short statistical review of chlorine production in the U.S.A. has been given by J. R. Skeen,[118] and W. R. Shearon, F. Chrencik and C. L. Dickinson[119] have described in some detail modern methods for the production of chlorine with caustic soda. J. V. Hightower[120] has also dealt with chlorine and caustic soda production, dealing particularly with a new plant at Houston, Texas, which uses undergound salt deposits and natural gas for cheap power and steam. Continuing the reviews of chlorine and alkali production, W. H. Shearon[121] has described the production in south-west U.S.A. and Mexico giving details of a sea-going tanker with nickel-lined holds for carrying concentrated caustic soda solution. On the other hand, H. F. Johnstone[122] has described at some length the non-electrolytic processes of chlorine production including oxidation of salt with nitric acid, and a revival of the old Deacon process. In a method patented by Phillips Petroleum Co.[123] for the production of chlorine, mixtures of hydrogen halides or organic halides with hydrocarbons are oxidized with hot dry air in the presence of a catalyst such as copper chromite. After drying, the exit gases go to a Deacon reactor and are oxidized with free oxygen to form chlorine and water. According to a patented method of the Standard Oil Development Co.,[124] chlorine can be produced by introducing gases containing hydrochloric acid into a reaction zone at 250°–400° c. and introducing iron oxide at a somewhat lower temperature. The ferric chloride particles formed move downwards into a second reaction zone at 500° c. where they are treated with oxygen or air, to give chlorine and to regenerate the ferric oxide. Chlorine and sodium sulphate are produced by reacting sodium chloride with sulphur trioxide at temperatures above 450° c., according to E. I. du Pont de Nemours & Co.[125] Another similar method for the production of chlorine and sodium sulphate is claimed by A. W. Hixson and R. Miller[126]; sulphur trioxide is treated with sodium chloride to form sodium chlorosulphonate, which is heated to give sodium sulphate, sulphur dioxide and chlorine. The sulphur dioxide and chlorine are liquefied and rectified, the chlorine being separated from the sulphur dioxide, which is catalytically oxidized to the trioxide and returned to the process. A cyclic process for the manufacture of the same two compounds has been patented by J. Kamlet[127]; in this case a mixture of sodium pyrosulphate and sodium chloride is heated to 325°–600° c. to produce sodium sulphate and a mixture of sulphur dioxide and chlorine, which is then passed with oxygen through a contact convertor with a vanadium catalyst to give a mixture of sulphur trioxide and chlorine, the former being converted to sodium sulphate.

A. Hoefle[128] has briefly described the liquefaction processes for chlorine and compared their relative merits. Solvay and Co.[129] have patented a method for separating gaseous mixtures of chlorine dioxide and chlorine by feeding them with air into a tower down which concentrated aqueous sodium chloride solution flows as a solvent while an inert gas such as air passes up the tower. The more soluble chlorine dioxide is removed at a low level whereas the less soluble chlorine is removed at a high level. The Air Reduction Co. Inc.[130] propose to concentrate dilute chlorine by absorption in water and re-vaporization at successively reduced pressures. By this method approximately one ton of chlorine/hr. (20% strength) can be produced with a steam consumption of 4·35 tons/hr. Another method of chlorine recovery is one patented by the Hercules Powder Co.[131]; in this method chlorine in mixtures with hydrochloric acid, air, water etc. is recovered by counter-current absorption at 20° C. with a suitable solvent in a packed Karbate tower, the rich liquor being subsequently stripped. Various devices for the safe handling of chlorine have been described by J. V. Hightower.[132] R. E. Hulme and A. B. Tillman[133] have critically evaluated the data of the vapour pressure, latent heat, specific volume, density and enthalpy of chlorine. The authors' results are sufficiently accurate for most engineering calculations. The uses of chlorine with special reference to the preparation of chloro-hydrocarbon solvents, inorganic compounds and chlorinated oils, have been reviewed by K. G. Mathur.[134]

A. J. P. Wilson and R. F. Warren[135] have reviewed briefly the American production of hydrochloric acid and the methods used. The combined rate of production from the 74 plants listed approaches one ton/min. The Fansteel Metallurgical Corporation[136] have patented a method for the manufacture of hydrochloric acid, in which gas containing hydrochloric acid is passed concurrently with water downwards on a heat-conducting wall in an apparatus made preferably of tantalum. Another method for hydrogen chloride manufacture is described in a Shell Development Co. patent[137]: hydrogen is treated with chlorine in an atmosphere of dry hydrochloric acid. By thus reducing the volume of reacting gases, the chamber walls can be kept sufficiently cool without the need for water cooling. A general method for the preparation of anhydrous halogen acids has been described in a patent issued to the Socony-Vacuum Oil Co.[138] Hydrogen or hydrocarbon reduction of metal halides results in the formation of anhydrous halogen acids. The metallic halides are made by the interaction of the free metal with moist waste gases containing air or oxygen and hydrochloric, hydrobromic, hydriodic or hydro fluoric acids. Another method for making anhydrous hydrogen chloride from aqueous solutions consists of treating the solution with concentrated sulphuric acid in a packed tower with injections of an inert liquefied gas which cools the sulphuric acid and strips the hydrochloric acid. This is described in a patent issued to the Phillips Petroleum Co.[139] C. F. Oldershaw, L. Simenson, T. Brown and F. Radcliffe[140] have described how hydrochloric acid containing up to 32–33% of HCl can be produced commercially in adiabatic towers by absorption of gases containing at least 10% HCl. The authors give theoretical data to show that the maximum concentration obtainable in adiabatic towers is 34·6% with a

feed gas containing 10 mol. % HCl. A plant is described which is producing 32% acid from gases containing chloromethanes. The Universal Oil Products Co.[141] have patented a method for purifying commercial hydrochloric acid gas by partial condensation, the gas phase being then treated with butane in the presence of aluminium chloride to leave a purified hydrochloric acid fraction. Gases containing a hydrogen halide can be recovered by passing them upwards through a descending stream of kerosene containing calcium sulphate on kieselguhr suspension, according to a patent by the Standard Oil Development Co.[142]; the hydrogen halide is then recovered by heating the carrier. In another patent[143] for the recovery of hydrogen halides, by the same company, the gases are passed through a slurry of copper sulphate in hydrocarbon oil and the hydrogen halide is subsequently recovered at 160°–190° c. F. P. Kerschbaum[144] has patented a method for concentrating gaseous hydrogen chloride by means of phosphoric acid. The Universal Oil Products Co.[145] have a patent for a process for the recovery of hydrogen chloride from exit gases containing hydrochloric acid and olefines; the gases are scrubbed with 35% aqueous hydrochloric acid solution to give a solution containing 45% HCl which is then extracted. In another patent[146] by the same company, hydrogen chloride is recovered from the gases from alkylation processes by passing them over a catalyst, consisting of aluminium chloride, at 130° c.

The American journal *Chemical Engineering*[147,148,149] has published a series of articles giving the action of hydrochloric acid of varying strengh upon construction materials. These include stainless steel, lead, rubber, silicon irons, carbon, tantalum, Chlorimet, iron and steel, precious metals, silicones, glass and nickel. K. Wickert[150] has investigated the effect of inhibitors, accelerators or retarders in pickling acids. The most effective pickling is obtained when the acid contains a balance between the inhibitor (reducing attack on the metal but not on the oxide), and the accelerator (increasing attack on the oxide to a greater extent than on the metal). A retarder to reduce attack on both is undesirable.

A British patent by J. N. Davis[151] describes the production of hypochlorous acid gas by decomposing liquid hypochlorite aerosols by carbon dioxide, with progressive disintegration by impact with solid objects. In a Mathieson Alkali Works Inc. patent[152] calcium hypochlorite is produced by neutralizing aqueous hypochlorous acid with crystals of the calcium hypochlorites, $Ca(OCl)_2$, $2Ca(OH)_2$ and $2Ca(OCl_2){\cdot}Ca(OH)_2$. Another method for making calcium hypochlorite has been patented by the Diamond Alkali Co.[153] An aqueous slurry containing calcium hypochlorite is vigorously agitated with gases containing carbon dioxide until all but 5% of the calcium hydroxide has been converted to calcium carbonate which is removed by filtration and the filtrate is spray-dried to give a product containing about 70% available chlorine. According to the Wyandotte Chemical Corporation,[154] high-test basic calcium hypochlorite can be produced by treating a solution of calcium hypochlorite and calcium chloride with aqueous caustic soda to precipitate the basic compound which settles out and can be separated. The Pennsylvania Salt Manufacturing Co.[155] have also a patent for producing basic calcium hypochlorite by chlorinating a suspension of calcium

hydroxide in aqueous sodium chloride, the resulting product being removed by filtration.

The Solvay Process Co.[156] have patented a method for the preparation of lithium hypochlorite by passing chlorine into a saturated aqueous solution of lithium hydroxide at 18° C. The resultant solution is concentrated until it contains 25% of lithium hypochlorite; then it is cooled and crystallized, the crystals being dried to yield a stable product. The Mathieson Chemical Corporation has a patent[157] for the purification of lithium hypochlorite in which water, lithium chloride and lithium chlorate are removed from the crude product by washing with tertiary butyl alcohol and then vacuum filtering. The alcohol is removed by a final wash with carbon tetrachloride.

There has been a further number of methods patented for the manufacture of chlorine dioxide. For example, the Mathieson Alkali Works[158] propose to react aqueous sodium chlorite with dilute chlorine and then to strip it in a tower with an inert gas. In another patent[159] by the same company, the chlorine dioxide is prepared by bubbling moist carbon dioxide through a layer of solid sodium chlorite, whereas yet another patent[160] proposes to produce chlorine dioxide from a mixture of sodium chlorite and phthalic anhydride by passing moist air over the mixture. Solid compositions[161] which generate chlorine dioxide on treatment with water are prepared from a chlorite and an organic acid anhydride together with a desiccant, such as calcium chloride. G. Holst[162] has compared the various methods for preparing chlorine dioxide by the reduction of chlorates dispersed in sulphuric acid with sulphur dioxide. J. Mouton[163] has reviewed the preparation, properties and uses of sodium chlorite, particularly in the textile industry. As regards the production of chlorite itself the N. V. Koninklijke Nederlandsche Zoutindustrie[164] have patented a method for producing chlorite by the absorption of chlorine dioxide in an aqueous alkali. The formation of chlorate is minimized by the addition of a suitable reducing agent such as compounds containing NH_2 or CN groups. In another patent for producing chlorites by the same company, the conversion of chlorine dioxide into the chlorite in alkaline solution is catalysed by a compound of such metals as silver, nickel, manganese, copper, cobalt, mercury, iron or gold or by the metal itself.

E. M. Harris[166] has investigated the causes of perchloric acid fires and concludes that the general causes are either contact of the acid with organic material or accidental formation of the anhydrous acid. Strict precautions are recommended such as buildings free from combustible materials, monthly examination of stocks with rejection or dilution of coloured acid and the use of safety clothing.

The extraction of bromine on a continuous plant has been described by J. J. Ronco[167] using native mineral springs containing 0·04 g./l. bromine. The hot water from these springs is acidified with sulphuric acid, treated with chlorine and the bromine expelled by air and absorbed in sodium carbonate solution. J. Mir[168] has described and illustrated the Kubierschky and Kaltenbach methods for recovering potassium chloride and bromine from brines.

The occurrence and production of iodine and its industrial applications

have been described by G. N. Imney.[169] An interesting quantitative study has been reported by A. Weissler and H. W. Cooper[170] of the ultrasonic production of iodine in aqueous potassium iodide solutions as an example of the mechanism by which ultrasonic radiation causes reactions. A commercial 'ultrasonorator' is described.

Alkali metal compounds

The cost and procedure of operating salt wells has been investigated by C. A. Butler[171] who used scale models made from large blocks of quarried salt. K. Takubowsky[172] has described the extraction of sea salt on the Black Sea coast by new methods including atmospheric evaporation favoured by the peculiar climatic conditions. An I.C.I. Ltd. patent[173] describes how calcium and magnesium can be removed from impure brine by precipitation with aqueous sodium carbonate solution and milk of lime, followed by settling and decantation. The purified brine is then evaporated. The production of sodium sulphate from the waters of Lake Chaplin by crystallization during the winter months has been described by A. A. Holland.[174]

According to an American patent[175] alkali metal salts can be decomposed into metal oxides and gaseous products by briquetting the salt with a supporting material such as iron oxide, heating *in vacuo* to decompose the salt and leaching to extract the alkali hydroxide. It is thus possible to decompose sodium sulphate into caustic soda and sulphuric acid.

In the field of electrolytic caustic soda production, N. Ramaswamy *et al.*[176] have described the purification and re-cycling of salt in the production of caustic soda from diaphragm cells. The process consists of washing the crude salt first with water and then with brine. H. C. Twiehaus and N. J. Ehlers[177] have described how caustic soda produced by electrolysis can be purified by means of counter-current flow of aqueous caustic soda and liquid ammonia in an extraction column under pressure, with continuous withdrawal of the upper liquid ammonia phase. Residual ammonia is removed from the caustic soda by flashing at reduced pressure and heavy metals are removed by absorptive agents. Another method[178] of purifying aqueous caustic soda consists of treating the impure solution with an alcohol, e.g. propyl, butyl or amyl, separating the immiscible alcoholic layer and agitating it with fresh water so that the absorbed caustic soda is converted into a high-grade solution and the alcohol is recovered for re-use. Aqueous caustic soda or caustic potash can be dehydrated in an insulated graphite tower while cascading over trays with a counter-current of steam at 260°–425° c.[179] Y. N. Nepenin[180] has studied the effect that sodium sulphide and sodium sulphate have on the conversion (by lime treatment) of sodium carbonate to caustic soda; both sodium sulphide and sodium sulphate decrease the degree of conversion, sodium sulphide to the greater extent. The American Viscose Corporation[181] have patented a method for reducing sodium sulphate to sodium sulphide, which is then treated with cuprammonium hydroxide to form caustic soda, aqueous ammonia and copper sulphide. According to the Wyandotte Chemical Corporation[182] dustless alkalis can be produced by the addition of about 2% of an ether such as the dimethyl ether of tetraethylene glycol.

Turning from caustic soda to the general alkali industry, H. Price[183] has described the development of this industry in Lancashire and Cheshire, while R. Williams[184] has described a Mexican plant for alkali production from lake brines. E. H. Boasson[185] has discussed the possibilities of developing the soda industry in Holland.

The American Potash and Chemical Corporation[186] have patented a method of seeding mixed sodium carbonate solutions to increase the ratio of the normal sodium carbonate. A. P. Belopolsky[187] has studied at some length the dependence of the velocity of carbonation of ammoniacal salt solutions on the partial carbon dioxide pressure of the carbonating gas and he has applied a theory of absorption to this carbonation process. The fall in velocity of carbon dioxide absorption at the end of the process is ascribed to a metastable state between the carbon dioxide, ammonia and the carbamate in solution. Sodium bicarbonate[188] can be produced in a two-stage cyclic process by bubbling carbon dioxide into a solution containing sodium chloride and ammonia at 20°–40° c. and the resultant bicarbonate is separated. After adding further sodium chloride and ammonia to the solutions, it is cooled to crystallize ammonium chloride which is removed leaving a solution of the original composition.

The production of sodium chromate with special reference to fusion diagrams has been studied by Y. E. Vilnyansky and D. I. Pudovkina.[189] The Chrome Chemical Pty.[190] propose to manufacture alkali metal chromates by roasting together in an oxidizing atmosphere chrome ore, lime and sodium carbonate. The calcination product is then cooled, and leached with water to dissolve out the sodium chromate. M. J. Udy[191] has patented a method for salting out sodium chromate from leaching liquor by the addition of up to 25–30% of caustic soda. During the manufacture of dichromates, sodium sulphate is obtained which contains chromium and heavy metals. According to the Diamond Alkali Co.[192] this impure salt can be purified by dissolving it in water, making the solution alkaline with caustic soda and then adding sodium sulphide. After filtration, the solution is aerated, neutralized with sulphuric acid and evaporated to recover pure sodium sulphate.

J. R. Skeen[193] has given his yearly summary of the U.S. production and consumption of sodium silicate. In the field of silicate production, the Wyandotte Chemical Corporation[194] have a patent for making crystalline anhydrous alkali metal orthosilicate by adding silica or soluble alkali silicates to a molten alkali hydroxide with continuous stirring.

Miscellaneous sodium compounds which have been mentioned are sodium arsenite, sodium tetrathionate and sodium ferrocyanide. The Pennsylvania Salt Manufacturing Co.[195] have a patent for manufacturing the first-named compound by stirring a hot concentrated solution of caustic soda with arsenic trioxide to form a granular mass which is then heated to 200°–250° c. and ground to a powder. According to a patent assigned to G. D. Searle & Co.,[196] sodium tetrathionate is purified by repeatedly washing with absolute ethanol or acetone and drying on a filter. E. I. du Pont de Nemours Co. in a patent[197] describe a method of production of sodium ferrocyanide by treating sodium cyanide with iron and blowing compressed air into the mixture.

The various stages in the development of the American potash industry[198] have been described. M. Prasad and G. V. Dange[199] have investigated plant and wood ashes as a potential source of commercial potash, while a Ministry of Supply report[200] describes processes for the recovery of potash from flue and cement dust. The recovery of potassium salts from sea water by adding a calcium salt of dipicrylamine and treating the insoluble potassium salt with dilute nitric acid has been described in a patent issued to the Norsk Hydroelektrisk Kvaelstofaktieselskab.[201] The production of potassium chloride and magnesium from carnallite and polyhalite is the subject of an American patent.[202] The polyhalite (potassium magnesium calcium sulphate) is leached with a crystallization mother-liquor containing calcium and potassium chlorides to precipitate calcium sulphate and the filtered solution is fortified with carnallite and treated with lime to precipitate magnesium oxide; the filtrate is cooled to crystallize the potassium chloride. A U.S. patent[203] issued to H. S. Colton *et al.* describes the production of potassium sulphate by the mixing and grinding of felspar and gypsum, and subsequent heating in an autoclave. The potassium sulphate is leached out with water. In a patent[204] of the International Minerals and Chemicals Corporation, langbeinite is hydrated by suspension in a potassium sulphate mother-liquor to form crystals of hydrated $K_2SO_4 \cdot MgSO_4$; these crystals are separated and treated with aqueous potassium chloride to precipitate the potassium sulphate and the mother-liquor is returned to the hydration step.

Potassium tetraborate[205] can be recovered from a solution saturated with $K_2B_4O_7.5H_2O$ and borax by adding potassium chloride; the potassium borate crystallizes out and is separated by centrifuging. Potassium pentaborate, $K_2B_{10}O_{18}.8H_2O$, on the other hand is prepared[206] by adding borax to water containing potassium chloride and treating the resultant sludge with carbon dioxide to precipitate the pentaborate which is separated by filtration or centrifuging.

Alkaline-earth metal compounds

A patent by the Hardy Metallurgical Co.[207] describes the preparation of alkaline-earth metal hydrides by treating the alkaline-earth metal salt of a phenol with hydrogen at about 18° c. and at 200 atm. pressure; phenol is regenerated.

In the washing of limestone to remove earthy matter wastage of water can be avoided by first washing with a slurry of the earthy matter and then with clean water. This method is described in a patent issued to I.C.I. Ltd.[208] W. S. Martin[209] has described the operation of a multiple hearth furnace drier operating in connexion with a high-temperature single hearth rabbling furnace for the calcination of precipitated calcium carbonate. A patent by G. & W. H. Corson Inc.[210] covers the bleaching of dolomitic calcium oxide by treatment with a sulphite compound which converts the harmful iron to a colourless ferrous compound. According to N. V. Knibbs,[211] impurities on the surface of quicklime can be removed either by mechanical attrition in a rotating horizontal cylinder or by hydration followed by removal of the powder. The

controlled calcination of hydrated dolomitic lime at 500° C. for 15 min. produces a material superior to ordinary dolomitic lime, according to a patent by the Permutit Co.[212] H. R. Staley and S. H. Greenfield[213] have determined the variations in the surface area of lime with the temperature of calcination. For a given time of burning a rise in temperature caused a decrease in surface area with a large increase in apparent density. T. I. Kumin and V. P. Uspensky[214] have studied the influence of certain factors on the viscosity of concentrated milk of lime. They found that the viscosity is least when it is made by the gradual addition of water to the dry hydrated lime. The viscosity increases with standing and with lime content and decreases with rate of flow. J. A. Hedvall *et al.*[215] have described the regeneration of gypsum from used plaster pottery moulds by calcination at about 900° C. In an I.C.I. Ltd.[216] patent, dehydration is effected by passing hot flue gases at 600° C. through a bed of hydrated calcium sulphate at 120°–140° C. at such a rate that the solid is maintained in a fluid state. The same method is claimed in a further I.C.I. Ltd. patent[217] for dehydrating gypsum.

The Socony-Vacuum Oil Co. Inc.[218] have described the manufacture of calcium carbide by heating lime in the presence of methane to give a complex which is subsequently fused at 1700° C. to yield a product containing 67% of calcium carbide.

Alkaline-earth cyanides[219] in the pure state can be prepared from the crude furnace product by treatment with anhydrous methanol and anhydrous ammonia. M. M. Fine[220] has described the concentration of calcium fluoride from tailings and waste rock by treatment with oleic acid and either sodium silicate or quebracho. Calcium chloride solutions are evaporated at 150°–200° C. by exposure to a gas in which the partial pressure of water vapour is less than one atmosphere.[221] The resultant granular solid contains 76–78% of calcium chloride. Solvay and Co.[222] have described in a patent the chlorination of milk of lime and treatment of this solution with lime to remove the calcium chloride and produce calcium chlorate.

J. B. Pearce[223] has patented a method for the manufacture of strontium oxide by heating strontium carbonate at 1200° C. with ashless carbon black in a partly sealed electric furnace. The resultant permeable strontium oxide is suitable for conversion to the peroxide. H. M. Busey and E. F. Pollard[224] have investigated the conversion of strontium sulphate to carbonate in sodium carbonate fusion and the effect of alkali halides. They found that calcium chloride and bromide had no effect while lithium chloride and bromide did inhibit slightly.

A U.S. Bureau of Mines Report[225] has described investigations which were carried out on the ore-dressing methods for barytes from New Mexico, and E. D. White[226] has described an American barytes plant giving a flow-sheet of the process. H. S. Booth *et al.*[227] have reported a series of experiments on the production of blanc fixe (barium sulphate) from barytes by solution in molten chloride and quenching in water, and secondly, the conversion of barytes to barium carbonate by heating with sodium carbonate. The production of barium carbonate from barytes and sodium carbonate is also described in a patent issued to G. and W. H.

Corson Inc.[228] In this method, the barytes is heated with a saturated aqueous sodium carbonate solution in an autoclave at 350 lb./sq. in. pressure for 3 hr.; 92% conversion is obtained.

A large amount of work appears to have been done on the production of magnesium compounds. In a Defence Plant Corporation patent[229] magnesite ore is ground, mixed with water and floated with an aliphatic acid to remove the siliceous matter. C. C. Brumbaugh[230] has described how dolomite can be calcined to the oxides of magnesium and calcium in a vertical kiln with a thermal efficiency of over 75%. The Marble-Head Lime Co.,[231] in their patent, separated magnesium oxide from calcined dolomite by selective carbonation with the direct addition of the calcined product to the carbonator without slaking. In a patented process of the Marine Magnesium Pròducts Corporation,[232] high yields of magnesium oxide from dolomite are obtained by eliminating caustic soda and the two-stage carbonation process; after calcining and slaking of the dolomite, the slurry is treated with magnesium bicarbonate, and flue gas is passed through to convert magnesium hydroxide to magnesium carbonate which is separated and calcined. Dolomitic limestone, when calcined at 1200°–1300° c., slaked and added to sea-water, precipitates magnesium hydroxide which is separated as described in a patent issued to the British Periclase Co., Ltd.[233] Dolomite can also be used for the production of magnesium thiosulphate and magnesium oxide. Thus the American Zinc, Lead and Smelting Co's. patent[234] describes the calcination of dolomite, suspension of the product in water and boiling with sulphur. The suspension is treated with sulphur dioxide and then with carbon dioxide. The precipitated sulphate and calcium carbonate are filtered off and the thiosulphate recovered by evaporation and crystallization. L. Minakata[235] has described the Pattinson and brucite processes for making magnesium salts, while in the Dow Chemical Co.'s patent[236] magnesium salts are prepared from sea water by passing the water through an ion-exchange agent, which is then regenerated by a saturated sodium chloride solution. The Idaho Maryland Mines Corporation[237] have patented methods for the production of magnesium oxide and magnesium sulphate from magnesium silicate. Another method making use of magnesium silicate for the production of magnesium oxide is described in a patent[238] issued to the American Zinc, Lead & Smelting Co. In this latter process dolomite and magnesium silicate are calcined and the resulting magnesium oxide is separated by extraction with carbonated water. In a patent by the Phillip Carey Manufacturing Co.[239] magnesium carbonate is prepared by the controlled heating of aqueous magnesium bicarbonate which has been prepared by carbonating a slurry of calcined dolomite. The next two processes for the manufacture of magnesium carbonates again use dolomite as the raw material. In the first of these,[240] the dolomite is crushed, calcined and wet-ground to convert most of the magnesium oxide into hydroxide. The slurry is treated with flue gas and saturated with carbon dioxide to form the aqueous magnesium bicarbonate,which is then treated with air to precipitate the normal carbonate. In the second process[241] dolomite after calcination and hydration is carbonated to form calcium and magnesium carbonates which are separated by froth flotation. Mixtures of magnesium and calcium carbonates can also be

separated by froth flotation using sodium naphthoxide as a collector for the magnesium carbonate.[242]

A precipitated magnesium silicate absorbing agent[243] is prepared by adding an alkali silicate to an excess of a magnesium salt to form a mixture from which gelatinous magnesium silicate is precipitated. The precipitate is prepared for use by drying, heating and grinding. According to the International Minerals and Chemical Co.,[244] magnesium chloride can be prepared from dolomite by calcination, slaking and separation by classification. Carbonation follows which precipitates calcium carbonate while the magnesium oxide is separated and treated with hydrochloric acid. Another method for making magnesium chloride, by the same company,[245] consists of the selective carbonation of slaked calcined dolomite, followed by acidification of the magnesium hydroxide–calcium carbonate slurry; this results in a purer quality of magnesium chloride. The Mathieson Alkali Works method[246] also uses calcined dolomite and the resulting magnesium oxide–calcium oxide mixture is hydrated in waste liquor from the ammonia–soda process and then treated with barium chloride to precipitate the sulphates. The slurry is carbonated to form calcium carbonate which is filtered off, the filtrate containing the magnesium chloride. Manganese and iron in magnesium chloride solutions can be precipitated by the addition of an alkali-metal chlorite according to another Mathieson Alkali Works Inc. patent.[247] The Dow Chemical Co.[248] produce magnesium chloride from sea water by precipitating magnesium hydroxide with excess lime and slurrying the precipitate with aqueous magnesium chloride. This is neutralized with hydrochloric acid and magnesium chloride is obtained as solid by evaporation. The International Minerals and Chemical Corporation[249] have described in their patent the production of magnesium chloride from serpentine, which is ground and treated with aqueous hydrochloric acid. The iron present is oxidized with hydrogen peroxide and precipitated by the addition of magnesium oxide. The filtered solution is evaporated and the solid salt is obtained by spray drying. If porous magnesium oxide is heated with coke in chlorine, it is possible to collected an uncontaminated molten magnesium chloride which passes downwards through the charge. A recovery of about 90% is possible by this method which has been patented by the Mathieson Alkali Works Inc.[250] A patent by the American Cyanamid Co. for the production of magnesium cyanide describes the addition of magnesium metal to a mixture of hydrocyanic acid and ammonia to form a double compound which is filtered off and heated at 180°–230° c.

Crude liquors containing zinc sulphate, iron and heavy metals can be treated with zinc dust to remove the heavy metals and then with calcium hydroxide and potassium permanganate which precipitate ferric hydroxide in an easily filtered form. This is described in a patent issued to E. I. du Pont de Nemours Co.[252] According to a patent of the Aluminium Co. of America[253] when finely ground beryllium ore is reduced at 1300°–2000° c. and then heated with magnesium fluoride at 1400° c., in the presence of aluminium oxide, beryllium fluoride is formed which can be purified mechanically or by fractional distillation.

Industrial gases

Pre-cooling and purification of gaseous mixtures before liquefaction can be achieved by passing the gas counter-current to a cold liquid in a scrubber, according to a patent by the British Oxygen Co. Ltd.[254] The Air Reduction Co. Inc.[255] have proposed to remove impurities from the gaseous feed to a liquefaction process by partly expanding the compressed and cooled gaseous feed, so that a small proportion of liquid is formed in which the impurities accumulate. Another patent, by the same company,[256] describes an apparatus for the recovery of gaseous nitrogen, oxygen and argon from air, leaving the impurities behind in the liquid. A third patent by the same company[257] describes the liquefaction and rectification of air in three stages, which together produce nitrogen, oxygen and rare gases.

D. W. van Krevelen[258] has described the technology of the nitrogen industry and J. F. Crockett[259] has dealt with the industrial uses of nitrogen and the rare gases. The purification of these rare gases by mixing the impure gas with a reactive gas such as hydrogen at 250° c. and 2000 lb./sq. in. pressure in the presence of activated alumina, is described in an Air Reduction Co. patent.[260] P. V. Mullins[261] has described the production of helium from natural gases containing 1·4% He, and W. A. Mays[262] has mentioned the use of 99·8% helium for welding.

The effect of the large-scale availability of oxygen on such processes as the Bergius and Fischer–Tropsch, Bessemer steel production, roasting sulphide ores and water gas production has been described by C. R. Downs.[263] P. Grassmann and G. Weiler[264] have reviewed recent literature on the U.S. oxygen production and B. H. van Dyke[265] has briefly described a plant for the large-scale production of oxygen. Emphasis is laid on the use of a new gas-to-gas heat exchanger made up from thin copper fin stampings. The use of an oxygen-enriched blast in furnace operation has been investigated by W. A. Haven[266] together with the economics of modern oxygen plants. According to a U.S. patent[267] an improved yield of oxygen is obtained if the reflux rate in the preliminary and final rectifiers is increased. The process patented by P. L. Kapitza[268] consists of producing a low temperature by adiabatic expansion of the residual gaseous phase of cooled partly liquefied air ; this low temperature is used to condense an oxygen-rich liquid from compressed air. In an electrolytic process for the production of oxygen, by the National Carbon Co.,[269] oxygen is produced in an electrolytic cell with the usual anode but no diaphragm and an active carbon cathode, capable of transferring air and of oxidizing the hydrogen formed to hydrogen peroxide or water.

For the production of ozone[270] it has been proposed to pass air over a unit consisting of two wire gauze electrodes separated by a dielectric. The high-tension potential on the surface of the electrodes effects the conversion of oxygen to ozone.

In a patent by the Hercules Powder Co.,[271] hydrogen is produced from hydrocarbons by mixing with steam and passing over a nickel catalyst at 650°–1095° c. to produce a mixture of hydrogen and carbon monoxide. On the other hand the Magnesium Metal Corporation Ltd.,[272] have proposed a process for producing hydrogen by reacting carbon monoxide

with steam in the presence of a suitable catalyst at 340° C. The residual hydrogen, however, contains 3% of carbon monoxide.

Carbon monoxide is produced according to an I.C.I. Ltd. patent[273] by burning coal or coke at a high temperature in oxygen-enriched air and reducing the amount of carbon dioxide formed by adding a small amount of a halogen or non-metallic halide. J. A. Tebboth[274] has investigated the reaction mechanism of the decomposition of carbon dioxide by nickel catalysts. It is stated[275] that economic temperature for the catalytic conversion of carbon monoxide by steam into carbon dioxide can be reduced by using a catalyst containing 0·2–0·5 copper, 0·1–0·5 magnesium oxide and 0·1–0·7 g. mol. alumina.

The present uses and methods of production of solid carbon dioxide have been reviewed.[276] The removal of carbon dioxide from gases by absorption in aqueous potassium borate, $K_2B_4O_7$, and its subsequent recovery by heating the resultant sludge, forms the subject of a patent by the American Potash and Chemical Corporation.[277]

For the storage or transport of acetylene or sulphur dioxide these gases may be dissolved in dimethyl sulphoxide according to a Swedish patent.[278] J. A. Lee[279] has described the direct synthesis on a large scale of hydrocyanic acid from purified air, natural methane gas and ammonia.

Miscellaneous

B. Orsoni[280] has described how the concentration of heavy water in water-electrolysis plants can be predicted mathematically and these predictions have been confirmed in commercial plants.

The Harshaw Chemical Co.[281] have patented the preparation of red copper oxide of pigment quality by heating copper oxide with sulphur and carbon in a non-oxidizing atmosphere at 650°–800° C. A later patent[282] on this subject by the same company substitutes copper sulphide for the carbon; in this case the heating is carried out at 650°–1000° C.

According to an American patent,[283] boron trichloride can be made by the high-temperature chlorination of boron trioxide and purified by passing through boron carbide at 800°–1000° C. and cooling. The recovery of boron fluoride, from gases containing it, can be effected according to an American patent[284] by cooling them, passing over lime, absorbing in sulphuric acid and heating this solution to recover the pure compound. In a patent by H. C. Smith,[285] borate tailings are refined by drying and calcining in the presence of basic oxides such as lime. H. I. Schlesinger *et al.*[286] have described a method for the preparation of pure boron coatings by heating in a static atmosphere of boron hydride.

The C. K. Williams Co.[287] propose to produce pigment-grade ferric oxide by heating ferrous sulphate monohydrate in a closed heating zone, while General Motors Corporation[288] propose to produce the same compound by subjecting granulated iron to the action of high-pressure steam. A process for making a readily filterable ferric hydroxide by treating ilmenite with ammonium fluoride is described in a patent issued to the Sherwin Williams Co.[289] P. de Lattre[290] has reviewed possible methods for the disposal of ferrous sulphate from waste pickle liquors and the Chemical Construction Corporation[291] have a patent for treating these

liquors with finely divided iron and crystallizing out the ferrous sulphate which can be dried or roasted. Another process for treating pickle liquor[292] consists of heating it to 145° c. under pressure, passing it into an enlarged pressure vessel and removing the resultant ferrous sulphate monohydrate precipitate. The treatment of waste copperas forms the subject of a patent by A. W. Whitford[293] who proposes to heat it in a modified Herreshoff furnace to yield ferric oxide, sulphur dioxide and sulphur trioxide.

A process for rendering nickel and cobalt or their alloys more readily soluble in acids by heating them with a sulphurizing agent is described in a patent by the Harshaw Chemical Co.[294]

Aluminium.—The preparation of alumina from bauxites and laterites has been briefly reviewed by P. Remy-Genneté.[295] A British patent by J. C. Seailles[296] describes the recovery of alumina from bauxite by roasting with calcareous material under either oxidizing or slightly reducing conditions. The roast is lixiviated with aqueous sodium carbonate and the residue mixed with more bauxite, re-roasted and extracted. These steps are repeated until the residue is sufficiently rich in iron to be used for smelting. S. Doldi[297] has described how the bauxite mud from the Bayer process can be calcined with sufficient sodium carbonate to form sodium aluminate, ferrate and titanate. J. Strachan[298] has described briefly the use of china clay for producing alum, alumina and aluminium, while alumina extraction from clay minerals by the lime sinter and lime soda sinter processes has been investigated by R. E. Grim *et al.*[299] The lime-soda sinter process for alumina from kaolin also forms the subject of patents by the Monolith Portland Midwest Co.[300,301] Another process for the extraction of alumina from clay, the ammonium sulphate process, has been investigated by W. R. Seyfried[302] and this same process is used in a patent issued to the Georgia Kaolin Co.[303] The technology of aluminium production from ferruginous clays has been investigated by three Russian authors, Y. Y. Dodonov *et al.*,[304] and J. M. Pertierra[305,306] has investigated the production of alumina from Spanish raw material (kaolins).

A. E. Williams[307] has discussed briefly the problems associated with the use of activated alumina as a drying agent. A British patent[308] claims that the adsorbent properties of alumina can be improved if it is heated to 300° c., thrown into a cold acid and then again heated to 350°–390° c. A patent by the Norton Co.[309] describes the manufacture of crystalline alumina by fusing it with 0·2–1% of a potassium or sodium compound and then pouring the melt into a large iron mould. Alumina gel can be made from amalgamated aluminium, according to a Standard Oil Co. patent,[310] by treating it with acetic acid and converting the resultant sol into a gel with an electrolyte such as ammonium carbonate, or weak acid. In an Aluminium Co. of America patent,[311] impurities are claimed to be removed from gelatinous aluminium hydroxide by washing with water, adding acid, drying, washing and re-drying.

Another patent by the Aluminium Company of America[312] describes how mixtures containing aluminium and alumina are heated with alkali carbonate to form the aluminate using excess of the carbonate to increase the yield. The same company[313] have also proposed to inhibit the

preparation of gelatinous organic sodium salts during the concentration of aqueous sodium aluminate by adding a small amount of rosin. The American Cyanamid Co.[314] propose to digest bauxite with excess caustic soda and neutralize the filtered solution with phosphoric acid. The product is dried and calcined to form a sodium phosphate aluminate useful in paper making and detergency. When crude calcium aluminate is to be dissolved in water, the process is facilitated by adding a small quantity of an alkali salt and an alkali sulphide, sulphate or chloride to inhibit solution of the silica.[315]

Aluminium halide sludges from isomerization processes are recovered by heating with sulphur; the halide is then volatilized from the residue and recovered as a crystallized solid.[316] According to the Standard Oil Development Co.[317] volatile metal halides are produced continuously by interacting a metal oxide with carbon and the free halogen; thus finely divided alumina suspension is heated with powdered coke in gaseous chlorine and the aluminium chloride is condensed. In the Phillips Petroleum Co. patent,[318] crude aluminium chloride is purified by boiling and then subliming at 1·5–2·5 atm. pressure. The electrolysis of aqueous aluminium choride between graphite electrodes with an asbestos diaphragm gives a high current yield of chlorine while vacuum evaporation of the catholyte gives a water-soluble alumina chlorine compound, this process being described in a U.S. patent.[319] A process for the production of aluminium sulphate patented by the Hercules Powder Co.[320] consists of digesting bauxite with sulphuric acid, treating the aqueous solution with sodium sulphide and then diluting with water to remove the iron.

E. A. Gee and W. K. Cunningham[321] have studied the production of iron-free aluminium sulphate for producing iron-free alum, on a laboratory scale, the greatest promise being shown by the method of adding cold ethanol to the hot aqueous aluminium sulphate solution. The same authors,[322] following through the production to the pilot-plant stage, were successful in obtaining pure alum crystals by the use of the ethanol process. The alcohol was recovered for re-cycling with an average loss of 3·1%. According to the Phelps Dodge Corporation patent,[323] potassium alum can be dehydrated by melting it in its water of crystallization, adding 1% of completely dry alum, heating until 35% of the water has been removed. It is then cast into shallow moulds, cooled, disintegrated, and passed through a rotary kiln.

Silicon, titanium and zirconium.—A number of references deal with the preparation of silica gel. Thus the Socony Vacuum Oil Co.'s patent[324] describes its preparation by precipitation with a strong acid, such as sulphuric, in the presence of a weak acid, such as phosphoric. In another patent,[325] the sodium silicate is atomized into an excess of violently agitated sulphuric acid; S. Koncar-Djurdjevic[326] has described silica gel production from asbestos. Apparatus for the continuous activation of silica gel in a warm dehydrating gas stream has also been described[327] and G. F. Jaubert[328] has described the use of silica gel for aero-engine protection. E. F. Meyer[329] has patented a method for making finely divided silica by adding sodium silicate to methanol and water, and neutralizing the finely divided suspension with carbon dioxide, to form

a suspension of silicic acid which is separated, washed dried and ground. A du Pont patent[330] describes silicic acid production from sodium silicate and sulphuric acid; the mixture is subsequently treated with triethyl phosphate to form a complex which is salted out and extracted with benzene to leave the polysilicic acid. In the Monsanto Chemical Co. patent,[331] acetone or ethanol is added to a silica aquasol containing dissolved inorganic salt which is thereby precipitated and removed.

E. I. du Pont de Nemours & Co.[332] have patented a process for preparing chlorofluorosilanes by bubbling silicon tetrafluoride through silicon tetrachloride and passing the gaseous mixture through a tube at − 60° c. The effluent gas is condensed at − 30° c. and the resulting condensate is fractionally distilled.

S. J. Johnstone[333] has described the distribution of titanium minerals and their subsequent conversion to titanium oxide pigments or metallic titanium and its alloys. According to a U.S. patent,[334] the most common titanium ore, ilmenite, can be converted into a condition suitable for sulphuric acid attack by mixing with a small quantity of naphthenic acid before grinding. R. Jonnard[335] has reviewed briefly the production of titanium oxide and titanium salts, and W. B. Blumenthal has described simple and rapid methods for producing chemically pure anatase and rutile, using an organic salt for anatase and titanium tetrachloride hydrolysed with ammonium sulphate for rutile.

There have been the usual large number of patents on titanium oxide. The American Cyanamid Co.[337] propose to prepare rutile by forming a rutile seed from hydrated titanium oxide which has been mixed with caustic soda, treated with hydrochloric acid and boiled. The National Lead Co.[338] have described a cyclic process in which ilmenite is extracted with hydrochloric acid and the concentrate chlorinated, dissolved and hydrolysed, the hydrochloric acid being re-used. The iron solution is reduced, neutralized with scrap iron and electrolysed. An addition to the chlorination process for making titanium oxide is another Pittsburgh Plate Glass Co. patent[339] where titanium tetrachloride is treated with hot oxidizing gases at less than 815° c. and remote from the hot surfaces. The resultant titanium dioxide is separated from the gaseous reaction products and calcined at 400°–750° c. Crude titanium tetrachloride for titanium dioxide production can be purified by refluxing with dry caustic soda, powdered antimony and water at 136° c. for 4 hours, followed by distillation, as described in a National Lead Co. patent.[340]

A number of patents have appeared on the production of zirconium compounds. The Titanium Alloy Manufacturing Co.[341] propose to prepare zirconium oxide by converting the zirconium ore into the oxysulphate which is washed with water and hydrochloric acid, and calcined at 900° c. to give the oxide. Another method of zirconium oxide production by the same company[342] consists in heating a mixture of zirconium and carbon in an electric furnace to form a compound which is afterwards spread in thin layers and ignited to form the oxide. A patented method[343] for making basic zirconium sulphate consists of evaporating a sulphuric acid solution of zirconium sulphate until it contains not less than 24% of zirconium oxide when the precipitated salt is separated. Iron can be removed from zirconium sulphate at a p_H of less than 7 by the addition

of calcium ferrocyanide.[344] In another method[345] double sodium-zirconium sulphates are obtained by fritting zircon sand with sodium carbonate and extracting the frit with sulphuric acid. After adjustment the solution is evaporated and crystallized.

Peroxy compounds.—In the field of hydrogen peroxide production, E. I. du Pont de Nemours & Co.[346] have patented a method for interacting hydrocarbon vapour with oxygen at 200°–550° c. In addition to hydrogen peroxide the reaction products are aldehydes and ketones. A suggested Dutch process[347] for the manufacture of peroxy compounds consists of agitating an amalgam of alkali and water which is saturated with oxygen. According to a Mathieson Alkali Works patent[348] relatively non-volatile impurities can be removed from hydrogen peroxide by evaporating at reduced pressure and condensing the vapours in two stages. It has been proposed by the Buffalo Electro-Chemical Co. Inc.[349] to treat 57% hydrogen peroxide with sufficient amyl borate to interact with the water present to yield an anhydrous solution of hydrogen peroxide in amyl alcohol, boric acid being precipitated. A design for closed containers for transporting high strength hydrogen peroxide, e.g. over 80% has been claimed by Laporte Chemicals Ltd.[350] This consists of an outer and an inner vessel with a space between them which contains sufficient distilled water to dilute the product to less than 60% hydrogen peroxide. Another Laporte Chemicals Ltd. patent[351] covers the manufacture of zinc peroxide by adding zinc oxide in successive small portions to hydrogen peroxide containing an acid such as sulphuric. In an I.C.I. Ltd. patent,[352] borax, sodium peroxide and hydrogen peroxide are mixed to form a homogeneous solution which is rapidly dehydrated to form a solid perborate product. A patent by the Mines Safety Appliances Co.[353] covers the use of potassium peroxide compositions for use in self-contained breathing appliances.

Chromium, molybdenum, tungsten and uranium.—S. Payno[354] has patented a method for heating crushed chromium ore with sulphuric acid to the reaction temperature after which it proceeds by its own heat, and the resultant chromium sulphate is oxidized to the trioxide electrolytically. According to the Pacific Bridge Co.,[355] chromium hydroxide may be produced by treating aqueous sodium chromate with sodium sulphide followed by carbon dioxide, the resultant chromium hydroxide being filtered off and washed. D. A. Peak[356] has underlined the precautions that should be taken when using chromium trioxide as an oxidizing agent.

Ammonium molybdate[357] can be reduced to molybdenum oxide by heating to 430° c. in a furnace, followed by treatment with steam at 630° c. and subsequent heating at 1050° c. in the presence of hydrogen. The U.S. Vanadium Co.[358] claims that molybdenum compounds for metallurgical purposes can be made non-dusting by heating the finely divided material at 700°–950° c. with a small quantity of flux such as an alkali carbonate.

A patent by G. Boericke[359] covers the preparation of tungsten compounds by heating the ore with water, caustic soda and bauxite in an autoclave at over 100° c. After filtration, the filtrate is treated with lime and again filtered, the filtrate being treated with more lime to precipitate calcium tungstate. The Shell Development Co.[360] have patented a

method for preparing tungsten compounds from spent catalysts by treatment with hydrogen sulphide and nitric acid and a French process[361] covers the purification of tungstic acid by solution in ammonia, evaporation, crystallization and precipitation with an acid.

M. Bachelet[362] has studied the separation of uranium salts in the treatment of betafite with acids and by alkali fusion. An E. I. du Pont de Nemours & Co. patent[363] covers the condensation of vaporized uranium halide and a patent by the U.S. Atomic Energy Commission[364] describes the preparation of uranium hydride by treating uranium at 150°–400° C. with hydrogen.

References

1 Skeen, J. R., *Chem. Engng. News*, 1948, **26**, 3410
2 Shapleigh, J. H. (Hercules Powder Corpn), U.S.P. 2,381,696
3 Odelhog, S.-O. B., B.P. 609,756
4 *Coke and Gas*, 1948, **10**, 391
5 Taylor, R. L., *Chem. Industr.*, 1946, **59**, 830
6 Otto, C. (Fuel Refining Corpn.), U.S.P. 2,435,898
7 Francis, C. B., U.S.P. 2,443,765
8 Gordon, K. and I.C.I. Ltd., B.P. 607,231
9 Shaw, J. A. (Koppers Co., Inc.), U.S.P. 2,386,985
10 McClenahan, F. M., U.S.P. 2,446,484
11 Schlain, D., Prater, J. D. and Ravitz, S. F., *Ind. Eng. Chem.*, 1949, **41**, 834
12 Audrieth, L. F. and Mohr, P. H., *Chem. Engng. News*, 1948, **26**, 3746
13 Spitz, A. W. *et al.*, *Chem. Engng.*, 1948, **55**, (5), 233, 236
14 Gilbert, N. and Daniels, F., *Ind. Eng. Chem.*, 1948, **40**, 1719
15 Tseitlin, A. N., *J. appl. Chem.*, *USSR*, 1946, **19**, 820
16 Union Chim. Belge Soc. Anon., B.P. 608,612
17 Datin, R. C. (Solvay Process Co.), U.S.P. 2,382,298
18 Scott, G. S. and Grant, R. L., *U.S. Bur. Min.*, *Inform. Circ.* 7463, 1948
19 Lonza Elektrizitätswerke & Chem. Fabr. A.G., B.P. 602,063
20 Amer. Cyanamid Co. and Stevens, A. H., B.P. 606,568
21 Green, H. D. (E. I. du Pont de Nemours & Co)., U.S.P. 2,387,577
22 Sporzynski, A., B.P. 608,885
23 Below, F., *Angew. Chem.*, 1947, **19**, **B**, 262
24 *Chem. Engng.*, 1948, **55** (8), 300
25 Sorel, J., *Chim. et Industr.*, 1948, **60**, 541
26 Hunter, F. R., *Amer. Inst. min. metall. Engrs.*, Tech. Publ. 2456, 1948; *Min. Technol.*, **12**, No. 5
27 Ellis, E. J. (Southern Phosphate Corpn.), U.S.P. 2,384,825
28 Davenport, J. E. and Hauman, J. F., *Amer. Inst. min. metall. Engrs.*, Tech. Publ. 2239, 1947 ; *Min. Technol.*, **11**, No. 6
29 Maust, E. J. (Coronet Phosphate Co., Inc.), U.S.P. 2,446,978
30 Skeen, J. R., *Chem. Engng. News*, 1948, **26**, 2436
31 de Witt, T. W. (Tennessee Valley Authority), U.S.P. 2,397,951
32 Silverstein, M. S., U.S.P. 2,440,303
33 Almond, L. H. and Steinbiss, H. K., *Chem. Engng.*, 1948, **55** (10), 105
34 Hignett, T. P., *Chem. Engng. Progr.*, 1948, **44**, 753
35 Idem, ibid., 895
36 Coleman, J. H. (Southern Phosphate Corpn.), U.S.P. 2,384,814
37 Idem, U.S.P. 2,384,813
38 Eyck, H. S. T., Chocholak, J. and Coleman, J. H. (Southern Phosphate Corpn.), U.S.P. 2,384,856
39 Shoeld, M. (Davidson Chem. Corpn.), U.S.P. 2,384,773
40 Soc. Anon des Manuf. des Glaces et Prod. Chim. de St. Gobain, Chauny & Cirey, B.P. 602,268
41 Bell, R. N., *Ind. Eng. Chem.*, 1948, **40**, 1464
42 Lee, J. A., *Chem. Engng.*, 1948, **55** (12), 126
43 Enterprise, R. and Moritz, J., B.P. 613,410

[44] Russell, C. H. (Monsanto Chemical Co.), U.S.P. 2,436,670
[45] Taylor, G. E. (Monsanto Chemical Co.), U.S.P. 2,390,400
[46] Partridge, E. P. and Texter, C. R., *Chem. Engng. News*, 1949, **27**, 840
[47] Albright & Wilson Ltd. and Inglis, G., B.P. 609,785
[48] Hall Laboratories Inc., B.P. 610,201
[49] Butt, C. A. (Internat. Minerals & Chem. Corpn.), U.S.P. 2,442,969
[50] Lange, W. and Livingston, R. (Ozark-Mahoning Co.), U.S.P. 2,423,895
[51] Menefee, A. B. and Greger, H. H., U.S.P. 2,429,477
[52] Odell, W. W. and Harbert, W. D. (Lion Oil Refining Co.), U.S.P. 2,389,810
[53] Flemming, E. P. and Fitt, T. C. (Amer. Smelting & Refining Co.), U.S.P. 2,388,259
[54] Idem, U.S.P. 2,431,236
[55] Fernelius W. C. and McReynolds, J.P. (Southern Acid & Sulphur Co., Inc.), U.S.P. 2,386,202
[56] Holmes, W. C. & Co., Ltd. and Cooper, C., B.P. 608,143
[57] Menefee, A. B. and Greger, H. H., U.S.P. 2,385,527
[58] Stirn, F. E. (Lederle Laboratories Inc.), U.S.P. 2,390,746
[59] Ulmer, R. C. and Churchill, J. F., *Chem. Engng.*, 1949, **56** (1), 95
[60] Hooker, G. W. and Landee, F. A. (Dow Chem. Co.), U.S.P. 2,384.378
[61] Hooker, G. W., Stowe, S. C. and Drake, L. R. (Dow Chem. Co.), U.S.P. 2,385,704
[62] Reid, W. S., *J. Metals*, 1949, **1**, Trans. Sect. 261
[63] Coster, N. W., Johnson, L. M. and Thieme, R. I., *Pulp Pap.* (*Mag.*), *Can.*, 1949, **23** (1), 34, 38, 41, 42, 44, 47
[64] Grace, W. T. and Muller, junr., J. C. (E. I. du Pont de Nemours & Co.), U.S.P. 2,445,112
[65] Wurz, O. and Wurz, E., *Papier, Darmstadt*, 1948, **2**, 190
[66] Bertetti, J. W. (Pan Amer. Refining Corpn.), U.S.P. 2,432,136
[67] Langen van der Valk, J. H. A. P. and Ruys, J. D. (Shell Development Co.) U.S.P. 2,441,521
[68] Mohr, A. C. (Stauffer Chem. Co.), U.S.P. 2,391,328
[69] Lilliard, J. G. and Pfenning, R. F. (Standard Oil Development Co.), U.S.P. 2,387,519
[70] Moltern, H. O. (Standard Oil Development Co.), U.S.P. 2,390,316
[71] Merriam, H. F. and Harkness, A. M. (Gen. Electric Co.), U.S.P. 2,389,070
[72] Merriam, H. F. (Gen. Chem. Co.), U.S.P. 2,389,071
[73] O'Shaughnessy, J. M. (Nat. Lead Co.), U.S.P. 2,394,470
[74] Gelfman, M. S., *J. appl. Chem., USSR*, 1947, **20**, 1160
[75] Kastens, M. L. and Hutchinson, J. C., *Ind. Eng. Chem.*, 1948, **40**, 1340
[76] Fanshaw, H. L., *Canad. Chem.*, 1949, **33**, 32
[77] Crawford, F. A. F., Bell, J. and Imperial Chem. Industries Ltd., B.P. 621,158
[78] Millett, H. C., *Chem. & Ind.*, 1948, 595
[79] Carter, B. M. (Gen. Chem. Co.), U.S.P. 2,394,426
[80] Luce, W. A., McHard, J. A., Scribner, L. R. and Mampe, E. P., *Chem. Engng.*, 1948, **55** (7), 227, 230, 232, 234, 234, 236
[81] Herstein, F. E., Roll, K. H., Luce, W. A. and Friend, W. Z., *Chem. Engng.*, 1948, **55** (8), 219, 220, 222, 224, 226, 228, 230, 232, 234, 236
[82] Fontana, M. G., *Ind. Eng. Chem.*, 1948, **40**, 87A
[83] Fairlie, A. M., *Chem. Engng.*, 1948, **55** (7), 109
[84] Dyson, W. H., *J. S. Afr. chem. Inst.*, **1**, 15
[85] Krebs & Co., Ltd. (Lanbi, O. and Gerber, M.), B.P. 618,548
[86] Clark, L. M. and Spittle, H. M., *J. Soc. chem. Ind.*, 1948, **67**, 5
[87] *Chem. Engng.*, 1949, **56** (1), 317
[88] Gamble, D. L., Cyr, H. M., Siller, C. W. and Bisbing, G. W. (New Jersey Zinc Co.), U.S.P. 2,443,383
[89] Avery, J. M. and Marek, L. F. (A. D. Little Inc.), U.S.P. 2,392,629
[90] Gamson, B. W. (Great Lakes Carbon Corpn.), U.S.P. 2,447,003
[91] Ferguson, R. P. (Standard Oil Development Co.), U.S.P. 2,443,854
[92] Standard Oil Development Co., B.P. 620,315
[93] Belchetz, A. (Stauffer Chem. Co.), U.S.P. 2,391,541
[94] Pechukas, A. (Pittsburgh Plate Glass Co.), U.S.P. 2,431,823
[95] Hallowell, A. R. and Vaala, G. T. (E. I. du Pont de Nemours & Co.), U.S.P. 2,393,247
[96] Merz., A. (Amer. Cyanamid Co.), U.S.P. 2,431,880

[97] Laury, N. A. and Lombardo, J. B. (Amer. Cyanamid Co.), U.S.P. 2,396,581
[98] Plaksin, I. N., Suvoroskaya, N. A. and Astafeva, A. V., *J. appl. Chem., USSR*, 1946, **19**, 668
[99] Canadian Copper Refiners Ltd. (Clark, C. W., Elkin, E. M. and Waitkins, G. R.) B.P. 608,080
[100] Standard Telephones & Cables Ltd., B.P. 603,877
[101] Saslaw, O. (Internat. Telephone & Radio Manufg. Corp.), U.S.P. 2,433,401
[102] Canadian Copper Refiners Ltd., B.P. 603,133
[103] *Chem. Industr.*, 1946, **59**, 1006
[104] Hamrick, N. T. and Voskuil, W. H., ibid., 1948, **63**, 942,974
[105] Finger, G. C. and Reed, F. H., ibid., 1949, **64**, 51
[106] Jones, A. G. and Imperial Chem. Industries Ltd., B.P. 620,745
[107] Batty, J. V., Havens, R. and Wells, R. R., *U.S. Bur. Min., Rep. Invest.*, 1947, 4139
[108] Wilson, A. J. P., *Chem. Engng.*, 1948, **55** (12), 313
[109] *Industr. Chem. chem. Mfr.*, 1948, **24**, 801
[110] Frey, F. E. (Phillips Petroleum Co.), U.S.P. 2,445,217
[111] Standard Oil Co., B.P. 605,472
[112] Hughes, E. C. (Standard Oil Co.), U.S.P. 2,386,798
[113] Idem. U.S.P. 2,440,542
[114] Kelley, C. S. (Phillips Petroleum Co.), U.S.P. 2,388,156
[115] Frey, F. E. (Phillips Petroleum Co.), U.S.P. 2,388,135
[116] Kassel, L. S. (Universal Oil Products Co.), U.S.P. 2,392,048
[117] Jones, O. C. (Monsanto Chem. Co.), U.S.P. 2,385,208
[118] Skeen, J. R., *Chem. Engng. News*, 1948, **26**, 2194
[119] Shearon, W. H., jun., Chrencik, F. and Dickinson, C. L., *Ind. Eng. Chem.*, 1948, **40**, 2002
[120] Hightower, J. V., *Chem. Engng.*, 1948, **55** (12), 112, 136
[121] Shearon, W. H., jun., *Chem. Engng. News*, 1948, **26**, 3474
[122] Johnstone, H. F., *Chem. Engng. Progr.*, 1948, **44**, 657
[123] Blumer, D. R. (Phillips Petroleum Co.), U.S.P. 2,395,314
[124] Murphree, E. V. (Standard Oil Development Co.), U.S.P. 2,436,870
[125] Iler, R. K. (E. I. du Pont de Nemours & Co.), U.S.P. 2,445,117
[126] Hixson, A. W. and Miller, R. (Chem. Foundation Inc.), U.S.P. 2,441,550
[127] Kamlet, J., U.S.P. 2,442,874
[128] Hoefle, A., *Angew. Chem.*, 1948, **20**, **B**, 206
[129] Solvay & Co., B.P. 611,224
[130] Balcar, F. R. (Air Reduction Co., Inc.), U.S.P. 2,447,834
[131] Bouchard, F. J. (Hercules Powder Co.), U.S.P. 2,393,229
[132] Hightower, J. V., *Chem. Engng.*, 1949, **56** (1), 96
[133] Hulme, R. E. and Tillman, A. B., ibid., 1949, **56** (1), 99
[134] Mathur, K. G., *J. sci. Industr. Res. India*, 1949, **8A**, 7
[135] Wilson, A. J. P. and Warren, R. F., *Chem. Engng.*, 1949, **56** (4), 305
[136] Hunter, F. L. (Fansteel Metallurg. Corpn.), U.S.P. 2,436,432
[137] Hill, E. S. (Shell Development Co.), U.S.P. 2,444,256
[138] Gorin, F. (Socony-Vacuum Oil Co. Inc.), U.S.P. 2,382,788
[139] Bottenberg, K. C. and Richardson, J. A. (Phillips Petroleum Co.), U.S.P. 2,437,290
[140] Oldershaw, C. F. *et al.*, *Chem. Engng. Progr.*, 1947, **43**, 371
[141] Pines, H. and Bloch, H. S. (Universal Oil Products Co.), U.S.P. 2,389,457
[142] Scmidl, A. J. (Standard Oil Development Co.), U.S.P. 2,397,760
[143] Wadley, E. F. (Standard Oil Development Co.), U.S.P. 2,397,768–9
[144] Kerschbaum, F. P. (Stowell, H. T.), U.S.P. 2,369,301
[145] Kassel, L. S. (Universal Oil Products Co.), U.S.P. 2,392,047
[146] Friedman, B. S. (Universal Oil Products Co.), U.S.P. 2,386,944
[147] Renshaw, W. G., Roll, K. H., True, O. S., Luce, W. A., *Chem. Engng.*, 1948, **55** (12), 231
[148] Scribner, L. R. *et al.*, ibid., 1949, **56** (1), 231, 232, 234, 236, 238, 240
[149] Rosenblatt, E. F. *et al.*, ibid., (2), 243, 244, 246, 248, 250, 252, 254
[150] Wickert, K., *Arch. Metallk.*, 1948, **2**, 56
[151] Davis, J. N., B.P. 608,140
[152] Soule, E. C. and Robson, H. L. (Mathieson Alkali Works Inc.), U.S.P. 2,429,531

[153] Cunningham, G. L. (Diamond Alkali Co.), U.S.P. 2,446,869
[154] Darbyshire, R. W. (Wyandotte Chem. Corp.), U.S.P. 2,436,745
[155] Spraner, J. W. (Pennsylvania Salt Manufg. Co.), U.S.P. 2,441,337
[156] Laue, K. E. E. (Solvay Process Co.), U.S.P. 2,384,629
[157] Robson, H. L. (Mathieson Chem. Corpn.), U.S.P. 2,443,618
[158] Woodward, E. R. (Mathieson Alkali Works Inc.), U.S.P. 2,388,202
[159] Hutchinson, W. S. (Mathieson Alkali Works Inc.), U.S.P. 2,394,064
[160] Aston, R. N. (Mathieson Alkali Works, Inc.), U.S.P. 2,436,134
[161] Mathieson Alkali Works Inc., B.P. 608,068, 608,069
[162] Holst, G., *Paper Tr. J.*, 1949, **128** (1), 21
[163] Mouton, J., *L'Ind. Textile*, 1948, **64**, 232, 257 ; *J. Text. Inst., Manchr.*, 1948, **39**, A.195
[164] N.V. Koninklijke Nederlandsche Zoutind, B.P. 603,338
[165] Idem, B.P. 612,615
[166] Harris, E. M., *Chem. Engng.*, 1949, **56** (1), 116
[167] Ronco, J. J., *Rev. Fac. Cienc. quim.*, 1945, **20**, 181
[168] Jesüs Mir, *Afinidad*, 1948, **25**, 351
[169] Emby, G. N., *S. Afr. industr. Chem.*, 1948, **2**, 66, 92
[170] Weissler, A. and Cooper, H. W., *Mfg. Chem.*, 1948, **19**, 505
[171] Butler, junr., C. A., *Chem. Industr.*, 1949, **64**, 48
[172] Takubowsky, K., *Chimia*, 1949, **3**, 33
[173] Crooks, D. A., Scott, T. R. and Imperial Chem. Industries Ltd., B.P. 617,137
[174] Holland, A. A., *Chem. Engng.*, 1948, **55** (12), 121
[175] Joudan, F. and Beeche, J., U.S.P. 2,446,595
[176] Ramaswamy, S., Kalyanam, N. and Narasimhan, A. R., *J. sci. industr. Res. India*, 1948, **7**, **B**, 93
[177] Twiehaus, H. C. and Ehlers, N. J., *Chem. Industr.*, 1948, **63**, 230
[178] Cunningham, G. L. (Diamond Alkali Co.), U.S.P. 2,446,868
[179] Ladd, E. T., U.S.P. 2,396,664
[180] Nepenin, Y. N., *J. appl. Chem., USSR*, 1946, **19**, 801
[181] Wicker, D. B. (Amer. Viscose Corpn.), U.S.P. 2,439,404
[182] Wegst, W. F., McNabney, R. and Bacon, L. R. (Wyandotte Chem. Corpn.). U.S.P. 2,390,466
[183] Price, H., *S. Afr. industr. Chem.*, 1947, **1**, 42
[184] Williams, junr., R., *Chem. Engng.*, 1948, **55** (8), 96, 136
[185] Boasson, E. H., *Chem. Weekbl.*, 1949, **45** (3), 33
[186] Suhr, H. B. and Firoh, E. B. (Amer. Potash and Chem. Corpn.), U.S.P. 2,392,888
[187] Belopolsky, A. P., *J. appl. Chem., USSR*, 1947, **20**, 1133
[188] Reindeers, W., B.P. 606,456
[189] Vilnyansky, Y. E. and Pudovkina, D. I., *J. appl. Chem., USSR*, 1947, **20**, 794
[190] Chrome Chem. (Aust.) Pty., B.P. 614,443
[191] Udy, M. J., U.S.P. 2,388,775
[192] Hirsch, A. (Diamond Alkali Co.), U.S.P. 2,392,669
[193] Skeen, J. R., *Soap*, 1948, **24** (12), 46
[194] Beecher, B. K. (Wyandotte Chem. Corpn.), U.S.P. 2,443,128
[195] Karr, E. H. (Pennsylvania Salt Manufg. Co.), U.S.P. 2,396,465
[196] Crosley, R. W. and Raymond, A. L. (G. D. Searle & Co.), U.S.P. 2,439,720
[197] Young, J. H. (E. I. Dupont de Nemours & Co.), U.S.P. 2,431,601
[198] *Agric. Chem.*, 1948, **3** (12), 25, 78
[199] Prasad, M. and Dange, G. V., *For. Res. Inst. Dehra Dun*, 1947, No. 95
[200] Ministry of Supply, 1948, Permanent Rec. Res. and Development Monograph II, 104
[201] Norsk Hydroelektrisk Kvaelstofaktieselskab, B.P. 605,694
[202] Sturbelle, L. S., U.S.P. 2,394,570
[203] Colton, H. S., Frischmuth, R. W. and Knowles, R. L., U.S.P. 2,430,863
[204] Barr, J. A. and Smith, W. A. (Internat. Minerals & Chem. Corpn.), U.S.P. 2,437,182
[205] May, F. H. and Suhr, H. B. (Amer. Potash & Chem. Corpn.), U.S.P. 2,395,567
[206] May, F. H. (Amer. Potash & Chem. Corpn.), U.S.P. 2,395,566
[207] Pechet, M. M. (Hardy Metallurgical Co.), U.S.P. 2,392,545
[208] Ratcliffe, A., Talbot, G. W. and Imperial Chem. Industries, Ltd., B.P. 612,075
[209] Martin, W. S., *Sth. Pulp Pap. Mfr.*, 1948, **11** (6), 86, 88, 89
[210] Minnick, L. J. (G. & W. H. Corson, Inc.), U.S.P. 2,434,710

[211] Knibbs, N. V. S., B.P. 610,498
[212] Calmon, C. (Permutit Co.), U.S.P. 2,442,584
[213] Staley, H. R. and Greenfeld, S. H., *Ind. Eng. Chem.*, 1949, **41**, 520, 522
[214] Kunin, T. I. and Uspensky, V. P., *J. appl. Chem., USSR*, 1946, **19**, 999
[215] Hedvall, J. A., Sandford, F. and Ahlberg, R., *Chalmers tek. Högskol. Handl.*, 1947, No. 60
[216] Franklin, R. G. and Imperial Chem. Industries Ltd., B.P. 610,439
[217] Arnold, M. H. M., Young, R. J. and Imperial Chem. Industries Ltd., B.P. 613,207
[218] Abrams, A. J. and Cook, L. B. (Socony-Vacuum Oil Co. Inc.), U.S.P. 2,380,008
[219] Christmann, L. J. and Houpt, A. G. (Amer. Cyanamid Co.), U.S.P. 2,386,434–6
[220] Fine, M. M., *U.S. Bur. Min., Rep. Invest.*, 1948, 4370
[221] Hedley, A. G. M. *et al.*, B.P. 612,603
[222] Solvay & Co., B.P. 615,438
[223] Pierce, junr., J. B., U.S.P. 2,382,909
[224] Busey, H. M. and Pollard, E. F., *Ind. Eng. Chem.*, 1948, **40**, 1988
[225] Fine, M. M. and Kennedy, J. S., *U.S. Bur. Min., Rep. Invest.*, 1948, 4280
[226] White, E. D., *Chem. Engng.*, 1949, **56** (4), 90, 128
[227] Booth, H. S., Pollard, E. F. and Rentschler, M. J., *Ind. Eng. Chem.*, 1948, **40**, 1981
[228] Minnick, L. J. (G. & W. H. Corson, Inc.), U.S.P. 2,440,641
[229] Woodward, H. S. and Bates, W. A. (Defence Plant Corpn.), U.S.P. 2,393,008
[230] Brumbaugh, C. C., *Chem. Engng. Progr.*, 1948, **44**, 881
[231] Wing, W. E. (Marblehead Lime Co.), U.S.P. 2,386,027
[232] Baker, E. B. (Marine Magnesium Products Corpn.), U.S.P. 2,442,481
[233] British Periclase Co., Ltd., Gilpin, W. G. and Heasman, N., B.P. 615,782
[234] Amer. Zinc, Lead & Smelting Co., B.P. 604,976
[235] Minakata, L., *Afinidad*, 1948, **25**, 529
[236] Grebe, J. J. and Bauman, W. C. (Dow Chem. Co.), U.S.P. 2,387,898
[237] Bradenburg, H. R. (Idaho Maryland Mines Corpn.), U.S.P. 2,384,008–10
[238] MacIntire, W. H. (Amer. Zinc, Lead & Smelting Co.), U.S.P. 2,393,920
[239] Greider, H. W. and MacArthur, R. A. (Philip Carey Manufg. Co.), U.S.P. 2,396,915
[240] Gloss, G. H. (Marine Magnesium Products Corpn.), U.S.P. 2,390,095
[241] Basic Refractories Inc. and Arnold, J. C., B.P. 610,817
[242] Basic Refractories Inc., B.P. 614,640
[243] Simons, O. F. (Floridin Co.), U.S.P. 2,393,625
[244] Lundin, H. (Internat. Minerals & Chem. Corpn.), U.S.P. 2,394,863
[245] Wrege, E. E. and Cunningham, W. A. (Internat. Minerals & Chem. Corpn.), U.S.P. 2,442,525
[246] MacMullin, R. B. (Mathieson Alkali Works), U.S.P. 2,393,115
[247] Hampel, C. A. and Weiler, J. E. (Mathieson Alkali Works, Inc.), U.S.P. 2,395,221
[248] Heath, S. B. and Minger, F. R. (Dow Chem. Co.), U.S.P. 2,398,743
[249] Butt, C. A. *et al.* (Internat. Minerals & Chem. Corpn.), U.S.P. 2,398,493
[250] Lepsoe, R. *et al.* (Mathieson Alkali Works, Inc.), U.S.P. 2,384,479
[251] Amer. Cyanamid Co., B.P. 609,731
[252] Waddell, M. C. (E. I. du Pont de Nemours & Co.), U.S.P. 2,369,270
[253] Willmore, C. B. and Chew, F. D. (Aluminium Co. of America), U.S.P. 2,387,203–7
[254] Brit. Oxygen Co., Ltd. and Schuftan, P. M., B.P. 615,683
[255] Dennis, W. (Air Reduction Co., Inc.), U.S.P. 2,431,866
[256] Idem, U.S.P. 2,443,508
[257] Van Duys, C. C. (Air Reduction Co., Inc.), U.S.P. 2,433,536
[258] van Krevelen, D. W., *Chem. Weekbl.*, 1948, **44**, 437
[259] Crockett, J. M., *Metal Progr.*, 1948, **54**, 833
[260] Balcar, F. R. (Air Reduction Co., Inc.), U.S.P. 2,384,065
[261] Mullins, P. V., *Chem. Engng. Progr.*, 1948, **44**, 567
[262] Mays, W. A., *Metal Progr.*, 1948, **54**,848
[263] Downs, C. R., *Chem. Engng.*, 1948, **55** (8), 113, 121
[264] Grassmann, P. and Weiler, G., *Chem.-Ing.-Tech.*, 1949, **21**, 19
[265] Van Dyke, B. H., *Steel*, 1948, **123** (12), 103, 134, 136, 140, 143, 146
[266] Haven, W. A., *Amer. Inst. min. metall. Engrs. Blast Furn., Coke Oven and Raw Mat. Proc.*, 1947, **6**, 50, 55; *J. Iron Steel Inst.*, 1948, **159**, 323
[267] DeBaufre, W. L., U.S.P. 2,380,417
[268] Kapitza, P. L., B.P. 614,006

[269] Janes, M. (Nat. Carbon Co.), U.S.P. 2,390,591
[270] Ozonair Ltd. and Cowell, E. F. W.. B.P. 603,662
[271] Hercules Powder Co., B.P. 610,078
[272] Magnesium Metal Corpn., Ltd., and Carter, A. G., B.P. 604,376
[273] Nonhebel, G., Arnold, M. H. M. and Imperial Chem. Industries Ltd., B.P. 606,321
[274] Tebboth, J. A., *J. Soc. chem. Ind.*, 1948, **67**, 62
[275] N.V. de Bataafsche Petroleum Maats., B.P. 609,166
[276] *Chem. Engng.*, 1949, **56** (2), 335
[277] May, F. M. (Amer. Potash & Chem. Corpn.), U.S.P. 2,395,564–5
[278] Aktieb Centrallaboratorium, B.P. 620,423
[279] Lee, J. A., *Chem. Engng.*, 1949, **56** (2), 134
[280] Orsoni, B., *Chim. e Industr.*, 1948, **30**, 232
[281] du Rose, A. H. and Robinson, C. F. (Harshaw Chem. Co.), U.S.P. 2,385,066
[282] Harshaw, W. J. and Harbert, C. J. (Harshaw Chem. Co.), U.S.P. 2,385,078
[283] Cooper, H. S. (Wilson, F. H.), U.S.P. 2,369,214
[284] Baldeschweiler, E. L. and Gaylor, P. J. (Standard Oil Development Co.), U.S.P. 2,381,027
[285] Smith, H. C., B.P. 614,030
[286] Schlesinger, H. I., Schaeffer, G. W. and Barbaras, G. D., U.S. Atomic Energy Comm., May, 144, MDDC–1338; *Battelle Libr. Rev.*, 1948, No. 6, 13
[287] Ayers, J. W. (C. K. Williams & Co.), U.S.P. 2,394,579
[288] Mann, C. A. (Gen. Motors Corpn.), U.S.P. 2,391,723
[289] Mayer, P. E. (Sherwin-Williams Co.), U.S.P. 2,429,209
[290] Lattre, P. de, *Sheet Metal Industr.*, 1948, **25**, 697, 716; *J. Iron Steel Inst.*, 1948, **159**, 441
[291] Allen, junr., L. N. and Zahray, W. K. (Chem. Construction Corpn.), U.S.P. 2,440,215
[292] Edge, D., U.S.P. 2,395,729
[293] Whitford, A. W., U.S.P. 2,433,498
[294] du Rose, A. H. (Harshaw Chem. Co.), U.S.P. 2,431,997
[295] Remy-Genneté, R., *Chim. et Industr.*, 1948, **60**, 336
[296] Seailles, J. C., B.P. 616,103
[297] Doldi, S., *Chim. e Industr.*, 1947, **29**, 140
[298] Strachan, J., *Paper Mkr., Lond.*, 1949, **117**, 164
[299] Grim, R. E., Machin, J. S. and Bradley, W. F., Illinois St. geol. Surv., 1945, Bull. 69; *Brit. Ceram. Abstr.*, 1946, 110A
[300] Anderson, F. J. and Williams, D. R. (Monolith Portland Midwest Co.), U.S.P. 2,438,488
[301] Monolith Portland Midwest Co., B.P. 601,968
[302] Seyfried, W. R., *Amer. Inst. min. metall. Engrs.*, Tech. Publ. 2473, 1948; *Min. Technol.*, **12**, No. 4
[303] Lyons, S. C. (Georgia Kaolin Co.), U.S.P. 2,388,983
[304] Dodonov, Y. Y., Medoks, G. V. and Soshestvenskaya, E. M., *J. appl. Chem. USSR*, 1947, **20**, 870
[305] Pertierra, J. M., *An real Soc. esp. Fis. quim.*, 1948, **44**, 251, 261
[306] Pertierra, J. M. and Lanza, F., ibid., B, 362, 369
[307] Williams, A. E., *Canad. Chem.*, 1949, **33**, 41
[308] Comp. de Prod. Chim et Electromet. Alais, Froges & Camargue, B.P. 604,947
[309] Norton Co., B.P. 607,689
[310] Heard, L. (Standard Oil Co.), U.S.P. 2,449,847
[311] Riesmeyer, A. W. and Stowe, V. M. (Aluminium Co. of America), U.S.P. 2,390,272
[312] Lynn, junr., L. S. and Shirley, E. L. (Aluminium Co. of America), U.S.P., 2,442,137
[313] Newsome, J. W., Heiser, H. W. and Wall, J. R. (Aluminium Co. of America), U.S.P. 2,440,378
[314] Lurie, D. (Amer. Cyanamid Co.), U.S.P. 2,431,946
[315] Seailles, J. C., B.P. 610,005
[316] Murray, M. J. (Universal Oil Products Co.,), U.S.P. 2,431,768
[317] Ferguson, R. P. (Standard Oil Development Co.), U.S.P. 2,446,221
[318] Arnold, P. M. (Phillips Petroleum Co.), U.S.P. 2,387,228
[319] Huehn, W. and Haufe, W., U.S.P. 2,392,531
[320] Brown, R. E. (Hercules Powder Co.), U.S.P. 2,394,660

[321] Gee, E. A. and Cunningham, W. K., *U.S. Bur. Min., Rep. Invest.*, 1948, 4191
[322] Cunningham, W. K., Gee, E. A. and Heindl, R. A., ibid., 1948, 4351
[323] Kingsbury, A. W. and Osborn, W. H. (Phelps Dodge Corpn.), U.S.P. 2,441,022
[324] Marisic, M. M. and Dray, S. (Socony-Vacuum Oil Co.), U.S.P. 2,386,810
[325] Internat. Minerals & Chem. Corpn., B.P. 615,581
[326] Koncar-Djurdjevic, S., *Bull. Soc. chim., Belgrade*, 1947, **12**, 129
[327] Litty, junr., F. L. (Davison Chem. Corpn.), U.S.P. 2,439,741
[328] Jaubert, G. F., *C.R. Acad. Sci., Paris*, 1949, **228**, 826
[329] Mayer, E. F., U.S.P. 2,386,377
[330] Robinson, J. W. (E. I. Du Pont de Nemours & Co.), U.S.P. 2,392,767
[331] Marshall, M. D. (Monsanto Chemical Co.), U.S.P. 2,391,253–5
[332] Hill, J. W., Lindsey, junr., R. V. and Wiley, R. H. (E. I. Du Pont de Nemours & Co.), U.S.P. 2,395,826
[333] Johnstone, S. J., *Indust. Chem. chem. Mfr.*, 1948, **24**, 750
[334] Kramer, E. N. (E. I. Du Pont de Nemours & Co.), U.S.P. 2,437,164
[335] Jonnard, R., *Rev. Quim. industr., Rio de Janeiro*, 1948, **17** (189), 16; (190), **16**; (193), 19
[336] Blumenthall, W. B., *Ceramic Age*, 1948, **51**, 320; *Brit. ceram. Abstr.*, 1948, 342A
[337] Cawenberg, W. J. and Tanner, junr., C. A. (Amer. Cyanamid Co.), U.S.P. 2,389,026
[338] Turner, J. L. and Plechner, W. W. (Nat. Lead Co.), U.S.P. 2,441,856
[339] Pittsburgh Plate Glass Co., B.P. 602,094
[340] Cole, S. S. and Meister, W. F. (Nat. Lead Co.), U.S.P. 2,396,458
[341] Wainer, E. (Titanium Alloy Mfg. Co.), U.S.P. 2,387,046
[342] Miller, J. B. (Titanium Alloy Manufg. Co.), U.S.P. 2,392,605
[343] F. W. Berk & Co., Ltd., and Chambers, F. W., B.P. 610,549
[344] Idem, B.P. 610,548
[345] Soc. de Prod. chim des Terres Rares, B.P. 606,681
[346] Harris, C. R. (E. I. Du Pont de Nemours & Co.,), U.S.P. 2,443,503
[347] N.V. Koninklijke Nederlandsche Zoutind., B.P. 606,745
[348] Richardson, C. N. (Mathieson Alkali Works, Inc.), U.S.P. 2,438,252
[349] Levitan, N. I. and Kuoch, R. (Buffalo Electrochem, Co. Inc.), U.S.P. 2,386,484
[350] B. Laporte, Ltd., Wood, W. S. Harnaman, J. and Bishop, C. O., B.P. 613,689
[351] Wood, W. S., Clennett, G. and B. Laporte Ltd., B.P. 607,445
[352] Imperial Chem. Industries, Ltd., B.P. 611,439
[353] Mine Safety Appliances Co., B.P. 611,587
[354] Payno, S., B.P. 619,134
[355] Parsons, T. (Pacific Bridge Co.), U.S.P. 2,431,075
[356] Peak, D. A., *Chem. & Ind.*, 1949, 14
[357] Rennie, R. F. (Westinghouse Electric Corpn.), U.S.P. 2,385,843
[358] U.S. Vanadium Corpn., B.P. 609,505
[359] Boericke, G. and Boericke, E. E., U.S.P. 2,390, 687
[360] Archibald, R. C. and Trimble, R. A. (Shell Development Co.), U.S.P. 2,386,081
[361] S.A. pour les Applications de l'Èlectricité et des Gaz Rares Ètabl. Claudepaz et Silva, B.P. 611,411
[362] Bachelet, M., *Bull. Soc. chim. Fr.*, 1947, **14**, 628
[363] Kraus, P. B. (E. I. Du Pont de Nemours & Co.), U.S.P. 2,446,181
[364] Newton, A. S. (U.S. Atomic Energy Commission), U.S.P. 2,446,780

CERAMICS, REFRACTORIES AND CEMENTS

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DURING 1949 certain trends in ceramic research which have become manifest since the end of the war have continued to receive emphasis and will, it is now clear, have a profound influence on the future development of the whole science of ceramics. One example is the increasing use of conceptions based on the ionic structure of solid and liquid phases in ceramics; this necessitates not perhaps so much a revision of existing knowledge as a re-interpretation in terms of ionic mechanisms. There are already indications, however, particularly in the fields of enamels and glazes, that the ionic approach may prove increasingly successful in producing fruitful generalizations having a direct application to the solution of practical problems. Attempts are also being made to familiarize the ceramist with the current ideas of crystal chemistry; e.g. Rigby[1] in an extensive paper on this subject has discussed the structures of the crystalline phases occurring in ceramic bodies, and the significance of vacant lattice sites. The possibility of using ceramics for high-temperature engineering applications has led to a new interest in the mechanical properties of ceramics at high temperatures and in the use of the 'special' highly refractory oxides and their compounds under conditions in which many other properties besides mere refractoriness are involved.

During the year considerable progress has been made towards the realization of the 'all-basic' open-hearth furnace as a commercial proposition in this country. Several trials of such furnaces have now been completed under strict technical supervision, while others are still proceeding. If unequivocal success cannot yet be claimed, the results are at least promising, and the wealth of technical information obtained will prove invaluable in the future.

On the border between refractory and fuel technology valuable investigations into the flow patterns of gases in furnaces, which have a direct bearing on refractory wear and on furnace design, are being carried out and papers have been published on gas flow in open-hearth furnaces[2,3,4] and in side-blown converters.[5] An outstanding feature of this work is the demonstration of the recirculation of the gases caused by the jet effect at burners and tuyères; in the case of the side-blown converter at least, there is evidence that this may be a major factor in refractory wear, which is a maximum just above the tuyères where the recirculating eddy strikes the side of the vessel.

The Proceedings of the International Congress on Rheology held in Holland in 1948 which is now published as a single volume contains papers of significance to all ceramists interested in the theoretical development of their subject. One paper of special interest is that by Houwink[6]; he shows that the suitability of plastic clay for modelling is due to its having a relatively high yield-value and a low coefficient of viscosity which is comparatively insensitive to temperature changes. It can therefore be formed readily, but retains the impressed form both at room temperature and on heating. Goodeve[7] has reviewed his theory of

thixotropy and plastic flow and illustrates the basic principle by means of a model in the form of a circular brush, the bristles of which engage one end of a loaded lever. On rotating the brush, the force exerted on the end of the lever by the bristles is found to be independent of the rate of rotation ; this illustrates his basic postulate that transfer of momentum by shear breaking of links of high energy content is independent of shearing rate. De Waele and Mardles[8] show that for suspensions of a given material in a series of liquids the specific viscosity and the sedimentation volume both increase as the 'wettability' decreases.

Crystal growth from the solid, liquid and vapour phase has been the subject of a discussion by the Faraday Society. Among the papers of direct application to ceramics was that of Barrer[9] who discussed the factors governing the growth of silicates. The hydrothermal crystallization of vitreosil at constant temperatures was discussed by van Praagh[10] and the hydrothermal synthesis of quartz from silica glass was described.[11] Lea and Nurse[12] describe crystallization processes occurring in slags and cements and a method which has been employed for the production of single crystals of $3CaO.SiO_2$ from melts consisting of mixtures of preformed $3CaO.SiO_2$, $2CaO.SiO_2$ and $CaCl_2$ so chosen that with loss of $CaCl_2$ they pass through the primary phase field of $3CaO.SiO_2$ in the ternary thermal equilibrium diagram. The final mixture consists of $2CaO.SiO_2$ and $3CaO.SiO_2$ but as the former 'dusts' on cooling it can be separated by washing with alcohol through a 300-mesh sieve. The growth of periclase crystals in magnesia refractories as a function of temperature and iron oxide content is also described.[13]

Phase relationships

Each year the list of phase equilibrium diagrams available to the ceramist increases. Testimony to the activity of research workers in this field is found in the fact that Hall and Insley have already found it expedient to add a Supplement to their 'Phase Diagrams for Ceramists.'[14] In this they take the opportunity to correct certain errors that occurred in the original text and they reproduce a number of diagrams which have been investigated since the original compilation was made. These include the diagrams of systems $BaO–B_2O_3$, $BeO–SiO_2$, $Li_2O–Al_2O_3–SiO_2$ and $K_2O–ZnO–SiO_2$ and revisions of the systems $SiO_2–ZrO_2$ and $Fe–Fe_2O_3$. The last-mentioned diagram, due to Darken and Gurry,[15] replaces one which was a modified form[16] of an early diagram due to Mathewson, Spire and Milligan. The chief alterations are in respect of the solubility of ferrous iron in Fe_2O_3 (which is now known to be very slight[17]), and the substitution of a peritectic reaction between wustite and magnetite in place of a eutectic, recent evidence favouring this form.

The system $BaO–B_2O_3$ has been found to contain four congruently melting compounds[18] : $BaO.4B_2O_3$ ($879 \pm 5°$ c.), $BaO.2B_2O_3$ ($900 \pm 5°$ c.), $BaO.B_2O_3$ ($900 \pm 5°$ c.), and $3BaO.B_2O_3$ ($1385 \pm 5°$ c.), the latter showing an inversion between 100 and 400° c. Mixes containing less than 30% BaO (wt.) separated on fusion at 868° c. into two layers, one containing 30% BaO, the other being nearly pure B_2O_3 ; the compounds $BaO.3B_2O_3$ and $2BaO.B_2O_3$ reported by previous workers were not confirmed. Foster and Royal[19] have reinvestigated the range from

$BeO.Al_2O_3$ (chrysoberyl) to Al_2O_3 of the system $BeO–Al_2O_3$. Previous workers had indicated the probability of a solid solution range from $BeO.Al_2O_3$ to $BeO.3Al_2O_3$ approximately. The present authors consider this incorrect, $BeO.Al_2O_3$ and $BeO.3Al_2O_3$ being two distinct compounds of definite composition. Morgan and Hummel[20] have studied the system $BeO–SiO_2$. To produce $2BeO.SiO_2$ (phenacite) it was necessary to seed with $2ZnO.SiO_2$ (willemite), phenacite being obtained by solid reaction after 5 hours' heating at 1500° c. On heating to 1560° c. it decomposed again to the oxides without the intervention of a liquid phase. A tentative diagram is proposed which shows phenacite to dissociate in the solid state at 1560° c. At higher temperatures a eutectic melting at 1670° c. occurs between BeO and SiO_2 and falls close to the silica boundary line.

An important modification to the phase diagram of the system $MgO–Al_2O_3–SiO_2$ is suggested by Riddle[21] who claims that a second ternary compound $4MgO.5Al_2O_3.2SiO_2$ (corresponding to natural sapphirine) has been discovered. According to the solid phase diagram proposed sapphirine coexists with mullite, spinel and cordierite; but there is apparently still some doubt as to whether it coexists with corundum or whether the join spinel–mullite occurs.

The (solid) phase distribution diagram of the system $CaO–Cr_2O_3–CrO_3$ has been investigated[22,23,24] on the basis of the stages detected in the dissociation on heating of calcium chromate in air and *in vacuo*. Four ternary compounds of CaO, CrO_3 and Cr_2O_3 have been identified, the molecular compositions in terms of these oxides being 9:4:1, 6:2:1, 4:1:1 and 3 : 2 : 2. Observed melting relationships are shown by means of a 'binary' diagram whose end members are CaO and Cr_2O_3, but in which the oxidized compounds $CaCrO_4$ 9 : 4 : 1 and 3 : 2 : 2 all occur at low temperatures in the solid state. Of these the 9 : 4 : 1 compound melts without dissociation at 1228° c. on heating in air so that mixtures of CaO and Cr_2O_3 containing between 40 and 60% CaO are of very low refractoriness under oxidizing conditions. Phase distributions corresponding to various stages of dissociation in the $CaO–MgO–CrO_3–Cr_2O_3$ quarternary system are also shown.

Phase distributions in the system $Na_2O–CaO–Al_2O_3–SiO_2$ have been given by Goldsmith[25] who also attempted to determine the thermal equilibrium relations for the join between $CaO.Al_2O_3$ and $NaAlSiO_4$ (nepheline or carnegieite).

Properties of clays and other raw materials

An important paper dealing with the influence of particle shape on plastic properties is that by Coughanour and Norton,[26] the ninth of a series on the fundamental properties of clays. The flow properties of suspensions of orthoclase, kaolinite, muscovite and halloysite lying between 0·4 and 0·8 μ. in size and representing cubic particles, thick plates, thin plates and lath-shaped particles respectively were studied in the dispersed and flocculated conditions. In the dispersed condition no yield-point occurred and no thixotropic behaviour was observed but the viscosity at a given concentration increased progressively from orthoclase to halloysite, i.e. with increasing anisometry of the particles.

In the flocculated condition thixotropic behaviour was observed with non-isometric particles and yield points occurred. The viscosity was, however, largely independent of particle shape owing, so the authors considered, to the formation of aggregates on flocculation, this nullifying the influence of the shape of individual particles.

Although the effect of particle shape may be considered to be largely hydrodynamical it is obvious that the nature and range of the repulsive forces between the particles when separated by moisture films will have a determining influence on plastic properties. In recent years considerable progress has been made towards the quantitative treatment of such forces considered to be due to the osmotic pressure exerted by the swarm ions in the electrical double layer round the particles. Schofield[27] in particular has succeeded in deriving an expression for the fall-off of the repulsive force with film thickness based on the treatment first attempted by Gouy. He has recently shown that his treatment can be extended to obtain values for the surface area of bentonite and kaolinite from measurements of negative adsorption and base-exchange capacity. For the bentonite he gets an area of 482 cm.^{2}/g. and for the kaolinite 16 cm.^{2}/g., the latter figure agreeing closely with estimates based on nitrogen adsorption and particle size determinations. Though he considers that the close agreement may be in part fortuitous, it is evident that his method has considerable promise.

Although the view that the base-exchange capacity of montmorillonite is due primarily to lattice substitution and should, therefore, be relatively independent of particle size is generally accepted, a dissentient voice has been raised by Johnson.[28] Using estimates of particle size and particle thickness obtained by centrifuging and by the electron microscope he calculates the area of the lateral surfaces of the plates, i.e. the surfaces normal to the *a* and *b* axes, and claims to show that the base-exchange capacity is proportional to this area and can be accounted for quantitatively by the number of broken bonds on these surfaces. These views are of considerable interest but it is clear that they will meet with considerable opposition, and his evidence will be subjected to close scrutiny by workers in this field. In particular the observation[29] that fine grinding tends to destroy the base-exchange capacity of montmorillonites appears to be in direct contradiction to Johnson's views, although here the conditions are rather different as there are indications that the grinding operations cause a breakdown of the lattice.

The relation between lattice expansion and hydration in montmorillonite and vermiculite has been discussed by Barshad.[30] The latter is essentially a mica in which Mg^{2+} or $Mg^{2+} + Ca^{2+}$ are the inter-layer cations instead of K^+, but with an expanded, hydrated lattice like that of hydrated montmorillonite. As with montmorillonite the Mg and Ca cations exchange readily, the exchange capacity being about 50% higher than that of montmorillonite. In the dried (but not dehydrated) state the inter-layer spacing is dependent on the nature of the exchangeable ion, the water content of the dried, natural material corresponding to two monolayers. The decomposition of a vermiculite and several micas has been investigated by Roy.[31] Like Gruner, he finds that approximately half of the water of the vermiculite (i.e. four molecules per unit

cell) was lost at 110° c. Most of the remaining water came off on prolonged heating at 330–350° c., talc being formed in the residue with no indications of lattice collapse along the *c*-axis. (Gruner had stated that talc was formed at 650° c. or 750° c.) Above 1050° c. the talc disappeared and spinel and three other unidentified phases were formed. Attempts at hydrothermal resynthesis of the vermiculite failed, and so did attempts to convert biotite hydrothermally to mica.

Because of their importance in industrial processes the changes taking place in clays on heating continue to occupy the attention of research workers and a detailed examination of certain alunite-bearing clays has been made by Gad and Barrett.[32] With their clays no potassium sulphate was formed on heating, the breakdown of dehydrated alunite leading directly to the formation of mullite with γ-Al_2O_3 at as low a temperature as 780° c. With further heating the latter changed to α-Al_2O_3 and finally at temperatures of over 1300° c. progressive decomposition of the mullite occurred leaving only corundum and glass, owing presumably to the effect of the alkali on the peritectic dissociation of mullite. They consider that the non-appearance of K_2SO_4 was due to interaction with silica of the dehydrated clay residue to form a potash–silica glass with progressive liberation of γ-Al_2O_3 from the residual network. Some confirmation of this was indicated by the fact that the upper endothermic peak on thermal analysis curves of such clays was found to be absent or very small, and by an observation made by a contributor to the discussion[33] that removal of silica from the dehydrated clay lattice by chemical means had caused the crystallization of γ-Al_2O_3 to take place at a lower temperature. The suppression of the exothermic peak by substances which combine with silica has also been observed by Gruver, Henry and Heystek.[34]

Murray and White[35] have attempted to study the thermal dehydration of clays as a kinetic process ; they find that the progress of the decomposition at constant temperature can be represented as a first order reaction up to some 80–90% decomposition. This has enabled them to evaluate velocity constants for the reaction at various temperatures and hence the energy of activation for the rate-determining step, which has a value of 34–38,000 cal./mol. for kaolinitic clays and a halloysite as against 57,600 cal./mol. for Wyoming bentonite. The values of the velocity constants obtained are consistent with the observed temperatures of the endothermic peaks on thermal analysis curves and with the known effect of heating rate on these peak temperatures.

Recently Grimshaw, Westerman and Roberts[36] obtained evidence from thermal analysis data that two distinct forms of tridymite may exist, each with its own characteristic inversion temperature, rather than a single form having two inversions; rather similar observations were made with cristobalite. Further evidence on these points has been obtained by Plumat.[37] He finds that cristobalite may occur in two distinct forms : a globular form inverting at 260° c. and a reticulate form inverting at 200° c. Tridymite also behaves as a mixture of two types, either or both of the inversions at 110° and 160° c. occurring. He considers that the final form is that inverting at 110° c., this being the more abundant in silica bricks after prolonged use. Still further testimony

to the complexities of the silica transformations is provided by the observations of Schulman, Claffy and Gunther[38] that, whereas silicic acid heated alone at 1050° c. gives cristobalite only, when heated in presence of calcium carbonate or calcium silicate it gives cristobalite plus quartz.

Considerable interest attaches to the analogies between aluminium orthophosphate ($AlPO_4$), which has acquired importance in piezo-electric work and in investigations into the cause of silicosis, and quartz. Beck[39] gives the stability ranges of the various forms as follows :

$$\text{Berlinite} \longleftrightarrow \text{Tridymite form} \longleftrightarrow \text{Cristobalite form} \longleftrightarrow \text{Fused } AlPO_4$$

Berlinite	Tridymite form	Cristobalite form
$\alpha \longleftrightarrow \beta$	$\alpha \longleftrightarrow \beta_1 \longleftrightarrow \beta_2$	$\alpha \longleftrightarrow \beta$
586 ± 2° c.	93 ± 3° c. 130° c.?	210 ± 5° c.

The transformations on heating are accompanied by thermal expansions similar to but rather less in magnitude than those associated with the corresponding silica changes. They also take place much more rapidly than the latter. No conversion of either of the high temperature forms back to berlinite has, however, yet been observed. Work on structural analogues of silica is also reported by Hummel[40] who has compared the expansion characteristics of cristobalite, carnegieite and Na_2CaSiO_4. The two latter minerals have structures based on the open cristobalite-type network, the carnegieite, however, representing partial filling of vacant sites in the network and the Na_2CaSiO_4 complete filling to give a close-packed structure. The observed expansions increase in the order cristobalite, carnegieite, Na_2CaSiO_4, i.e. with progressive filling of the lattice.

Ceramic bodies and making processes

A useful addition to the comparatively small number of authoritative books on ceramics is E. Rosenthal's 'Pottery and Ceramics.'[41] Though intended for the layman (it is published in the Pelican series) it contains much that should interest the specialist.

It has long been accepted that the improved workability of clay resulting from storage is due, in part at least, to bacterial growth, and the fact that casting slips after storage generally require additional electrolyte to prevent agglomeration of the colloids has been attributed to effects of this kind. The reverse effect has been observed in certain slips[42] which appeared to become considerably more dispersed on storage ; this showed up in a rate-of-cast test as a decrease in the weight cast. When an inorganic acid (sulphuric) was substituted for the acetic acid used in preparing the slip the trouble disappeared, showing that the promotion of bacterial growth by the organic acid had been responsible. An investigation into the effect of methods of slip preparation on the dry and fired properties of cast bars of high-voltage electrical porcelains is also reported.[43] Of the factors investigated, it was found that wet ball-milling had the most marked effect on dry and fired properties. Further investigation showed that the increased dry strength was mainly due to ball-milling of the plastic constituents while increased fired strength and decreased water absorption after firing to cone 11 was primarily due to milling of the fluorspar and flint.

The development of a new mineral, sierralite, for use in the production of cordierite bodies is reported.[44] Sierralite is a hydrous aluminium silicate, shown by X-rays to be a chlorite, and containing approximately 36% SiO_2, 24% Al_2O_3 and 23% MgO. A 50/50 mix with Florida kaolin gave a calculated composition closely approaching theoretical cordierite; after firing to 2350° F. it gave a coefficient of expansion of $1{\cdot}11 \times 10^{-6}$ from room temperature to 600° C. Both with this mix and with similar mixes of sierralite and ball clay trouble was encountered owing to the well known short firing-range of high cordierite bodies. It was found, however, that zircon additions of up to 20% effected a considerable improvement, decreasing the shrinkage and enabling the firing temperature to be increased by 50° F. Another attempt to overcome the short firing-range of cordierite bodies compounded from mixtures of clay, talc, alumina and magnesia is described.[45] Successful bodies having a reasonable firing-range were produced by blending precalcined mixtures of the above constituents.

The successful development of a permanently-sealed high-vacuum tube for a betatron has been described,[46] the shape of the tube being such that to make it in glass presented considerable difficulties. A suitable body composition was 15% English ball clay, 40% English china clay 25% felspar and 20% flint, which gave good all-round properties and a uniform rather than a minimum thermal expansion to 700° C. A low-expansion glaze containing beryllia was also developed; the glass selected for sealing into the tube was one used for sealing to tungsten, its thermal expansion curve fitting fairly closely to those of the body and the glaze up to 500° C. Tubes of this type are now in production.

A study has been made[47] of the crystalline phases developed in kaolin–flint–felspar bodies, using the Geiger-counter X-ray spectrometer. Free quartz (with cristobalite) was found in most of the fired mixtures, but decreased with increasing firing time and temperature. The mullite content, on the other hand, increased with increasing clay content at constant felspar/flint ratio and with increasing time and temperature owing to increasing reaction between the constituents. With increasing felspar content the general trend was a decrease in the amount of crystalline material. The addition of whiting caused mullite ultimately to disappear, wollastonite appearing as a phase; wollastonite and mullite should not, of course, coexist at equilibrium. The addition of $MgCO_3$ apparently gave no new crystalline phases but reduced the quartz content more markedly than lime addition did. Substitution of nepheline-syenite for the potash felspar caused a considerable decrease in free quartz at the lower time and temperature of firing, but at higher temperatures there was little difference between the two types of body in this respect.

In the field of electrical porcelains it is now recognized that with alkaline-earth titanate bodies the optimum electrical characteristics are obtained when the body remains heterogeneous after firing.[48] This is the principle underlying several patents which prescribe that the final body should be prepared by sintering powdered mixtures of previously prepared titanates.[49,50] Bunting, Shelton and Creamer[51] have followed

up their systematic investigation of compositions in the system $BaTiO_3$–$4MgO : TiO_2$–TiO_2 with a similar investigation of the system $BaTiO_3$–$3CaO : TiO_2$–TiO_2. As in their previous works they found that considerable deterioration in the electrical properties could occur on exposure to the atmosphere. With changing composition the value of the dielectric constant varied from 34 to several hundreds in the region of $BaTiO_3$. Q values also showed a wide variation, being lowest in the compositions of high BaO content.

F. H. Riddle[21] has described the history of the development of sparking-plug porcelains from the early days of flint–felspar–clay and talc–clay bodies to the present. Clays were abandoned, because of non-uniformity of the product, in favour of 100% non-plastic bodies bonded with plastics having a suitable combination of thermoplastic and thermosetting properties. Later the need for improved thermal shock resistance led to the elimination of flint; calcined clay, synthetic mullite and sillimanite minerals were used instead. To improve the electrical properties an attempt was made to eliminate alkalis by replacing felspar with alkaline-earth minerals. Finally the development of the modern corundum body, with its increased lead resistance, took place; early troubles encountered in Germany were overcome by the use of higher firing temperatures and by substituting highly sintered soda-free alumina for the highly crystalline, electrically fused material used by the Germans. At present sparking-plug manufacturers are interested in a wide variety of materials, future developments being undertaken with applications of ceramics to the jet engine and the gas turbine in view.

Glazes

Ryder[52] has recently made the point that the differences between glazes and enamels can be considered as functional rather than fundamental. Thus while the 'fit' between enamel and the base iron or steel requires a coefficient of expansion of $8–12 \times 10^{-6}$ per °C., the coefficient of expansion of glazes is normally of the order of $3–7 \times 10^{-6}$. The firing temperature of enamels is restricted by the need for avoiding sagging and warping of the base metal and it is normally between 700 and 900° C., the duration of the firing cycle being 10–20 min. Pottery glazes on the other hand are required with firing temperatures varying between 950 and 1350° C. (leaving out low-fire lead glazes and high-fire glazes for special porcelains); the firing cycle usually extends over many hours. Glazes firing at the lower end of this range still frequently contain lead oxide as a major constituent, mainly because of the excellent gloss obtainable with it; lead has been largely eliminated from enamel compositions. Glazes are normally compounded from a prepared frit which is milled with such additions as china clay, Cornishstone, felspar, flint, etc. When opacification is required the opacifiers, which at present include SnO_2, ZrO_2 and zircon, are always added at the mill. Colours are normally applied before glazing in the form of coloured clay slip or engobe, which is then covered with a transparent glaze. Tin oxide is still preferred for bright or glossy opaque white glazes, and it is used with other opacifiers in the semi-mat or satin glazes. Mat opaque glazes usually depend on the development of micro-crystalline precipitates

of silicates and aluminosilicates of Ca, Mg and Zn often with TiO_2, ZrO_2 or zircon, and they require strict control of firing and particularly of cooling conditions.

On the whole, investigations of opacification in glazes have tended to lag considerably behind what has been done in the enamelling field. An investigation to develop a white, opaque, low-expansion glaze for a zircon porcelain having an expansion coefficient of $4{\cdot}36 \times 10^{-6}$ has, however, been described recently by Luttrell.[53] Preliminary adjustments to the composition were made from trials with compositions based on blends of the 'zirconium silicates' of Mg, Ca and Zr, that of Ba being discarded as it gave unsatisfactory gloss. Finally glazes of reduced lime content but otherwise similar to the best of the earlier series were prepared from the raw materials without the use of the double silicates. On the usual molecular formulation it was found that the best glazes had less than 0·20 equivalents of KNaO, the rest of the RO group, totalling 1·00, being alkaline-earth oxides of which the MgO was between 0·40 and 0·50 equivalents. Al_2O_3 and SiO_2 were from 0·3–0·4 and 3·0–4·0 equivalents respectively, with ZrO_2 from 0·5–0·7 equivalents, B_2O_3 being limited to 0·2.

An investigation of the relation between glaze-body stresses and the thermal properties of white-ware bodies has also been described.[54] A close correlation was found between the stress characteristics as shown by the glaze-fit ring test and the thermal expansion differential between glaze and body. The 10% porosity body gave the best results in the thermal shock test. A new type of overglaze transfer which has been described consists of vitrifiable enamel on a film of collodion to which a backing paper is attached by a water-soluble adhesive.[55,56] Care must be taken during firing to burn off the carbon before vitrification begins. The colouring agents used by the early Chinese potters have been the subject of a note by A. L. Hetherington.[56]

According to current views on glass structure the cations present can be classified as network-formers : Si^{4+}, B^{3+}, P^{5+}, Al^{3+}, etc. (though Al_2O_3 itself does not apparently form a glass) ; and network-modifiers : Na^+, K^+, Ca^{2+}, Ba^{2+}, Pb^{2+}, etc., which are of large size and small charge. Though Pb^{2+} belongs to this latter group, it is possible to obtain stable lead glasses with up to 80% of lead oxide in them. The reason for this is that Pb^{2+} has not the noble-gas structure and is highly polarizable. There is, therefore, a strong mutual polarization of Pb^{2+} and O^{2-} ions, and the individuality (as separate ions) of Pb^{2+} and $(SiO_4)^{4-}$ is greatly diminished. Glasses of high O : Si ratio can thus be formed, though they are structurally considerably weaker than those containing chiefly glass-forming cations, and they are more susceptible to chemical attack. To strengthen them it is necessary to lower the ratio of oxygen ions to glass-forming ions to restore the continuous network structure of the more siliceous glasses. This can be done by introducing, as oxide, a tervalent glass-forming ion which takes up a tetrahedral co-ordination with regard to oxygen in glasses of this type. Al^{3+} is such an ion, so that the introduction of Al_2O_3 into lead bisilicate frits either as an addition, when the lead concentration is reduced, or as a replacement for SiO_2 with suitable adjustments of the PbO, should increase the resistance of such frits to chemical attack.

An interesting, and apparently successful, application of these principles to the solution of a very practical problem is described.[58] In a tile factory it was found that the ammonium chloride used as a deflocculant was causing excessive volatilization of lead from the glaze during firing, resulting in the appearance of certain characteristic faults in the glaze. Though the use of ammonium chloride was discontinued, there was still sufficient in the kiln atmosphere to cause the fault to persist. The addition of 4% Al_2O_3 to the lead borosilicate glazes, however, reduced the incidence of the trouble until the atmosphere had cleared, when the normal glaze was used again. Experiments in concentrated ammonium chloride atmospheres with treated and untreated glazes demonstrated clearly the protective action of the Al_2O_3 on the lead of the glaze.

One effect of removing PbO from a $PbO–SiO_2$ glaze is that the surface tension increases. It follows from this that there will always be an excess of PbO in the surface of such glazes. This aspect has been discussed recently,[59] and it has been shown that, in $ZnO–B_2O_3$ melts, ZnO raises the surface tension (beyond the range of liquid immiscibility); this favours concentration of B_2O_3 in the surface and consequently increased volatilization-loss of B_2O_3. Surface-tension effects are also responsible for the tendency for chrome-red glazes to spread into surrounding colourless glazes, the presence of CrO_3 causing a marked lowering of surface tension.[60] Chromate ion, therefore, tends to spread over the surface of the neighbouring glaze.

Enamels

It is now fairly generally accepted that a major cause of colour variation in titania-opacified enamels is variation in the particle size of the crystallizing phase, which may be either anatase or rutile, though rutile tends to predominate. This duality of form has been recognized as a barrier to the attainment of complete control over colour; higher firing temperatures, which favour rutile and increased particle size, lead generally to creamy tones. An important investigation of the factors influencing the crystal form of the precipitated TiO_2 has been described by Millar.[61] He finds that reduced, high-titania enamels, which contain oxygen-deficient titania, always produce rutile on re-oxidation. Again any undissolved TiO_2 in the enamel at high temperatures will always be present as rutile, which will nucleate the crystallization of rutile from the melt on cooling. Similarly, inefficient quenching of the frit will allow premature crystallization of rutile at high temperatures. To produce anatase, therefore, it is necessary that the melt should be completely 'batch-free,' that quenching should be efficient and that firing should be carried out under completely oxiding conditions, the firing time and temperature being kept to a minimum. He gives the composition of a frit which can be smelted at 1200° C. and which after firing between 800 and 850° C. is opacified by anatase. The crystal size of the anatase, it has been found, increases much more slowly than that of rutile on prolonged firing. To obtain cold, neutral whites the precipitated TiO_2 should therefore be in the form of anatase.

Other work with a bearing on the colour variability of titania enamels has been carried out. Marbaker, Saunders and Baumer[62] show that

the slump properties, reflectance, colour value and colour stability (rate of change from blue to yellow tones with increased firing temperature) are all influenced by the electrolytes used to disperse the clay. Cook and Essenpries[63] studied the effects of total alkali content, Na_2O/K_2O ratio and replacement of Na_2O and K_2O by Li_2O on reflectance. In lithia-free enamels containing 9–15% alkalis the best results were got with a high Na_2O/K_2O ratio. Lowering the ratio decreased the fluidity and shifted the colour towards blue, whereas with values of the ratio less than unity the reflectance decreased. Substitution of K_2O by Li_2O on a weight for weight basis improved reflectance and increased the rate of crystallization of TiO_2, shifting the colour towards yellow. The influence of the form in which Li_2O is added has also been studied[64]; lithium silicate gives, it is claimed, the best properties whether added to the smelter or the mill. Similarly Coffeen[65] has concluded that barium and potassium antimonates are the most satisfactory substitutes for the more commonly used sodium antimonate in antimony-opacified enamels.

Development work on vitreous enamels for aluminium is still proceeding. In preparing the metal strict adherence to the procedure laid down is necessary, acid treatment followed by pre-treatment with a chromate solution preceding application of the enamel.[66] The coatings at present available are apparently not very resistant to slow moisture penetration, nor to acid or alkaline attack, but this weakness is being overcome.[67]

The problem of producing a single-coat white enamel with satisfactory adherence, and with the necessary gloss, colour and reflectance is not a simple one as it involves close control over the metal composition, the frit and the enamelling operation. In particular, thorough cleaning is necessary and a nickel dip has usually been considered advisable to promote adherence; to minimize boiling the use of steels containing titanium, which stabilizes the carbide, is generally advocated.[68,69,70] High firing temperatures are in general conducive to excessive boiling so that it is an advantage to use an enamel of low maturing temperature provided that hardness and acid resistance are not impaired. These and other aspects of the problem have been discussed by King and Stull[71] who give four frit compositions suitable for direct application.

The effect of mill additions of silica, felspar and nepheline-syenite on the molten viscosity of steel ground-coat enamels using a concentric cylinder apparatus is described.[72] All three additions raised the viscosity, the effect of silica being the most marked. It is of some interest that of the three speed–deflection curves shown two indicate Newtonian flow, while the third shows curvature corresponding to an increase in the viscosity coefficient at low rates of shear.

Resistance to weathering of enamels in receiving considerable attention in the U.S. Harrison and Moore[73] have now reported on their examination of test pieces exposed for seven years to various outdoor atmospheres. (They previously reported on the samples after one year's exposure.[74]) They find that although salt-air conditions were worse than inland urban conditions, where coverage was complete, there was perfect protection of the underlying metal in all cases. Where coverage was poor, e.g. at supporting lugs, considerable corrosion occurred. Sweo[75] has endeavoured to find a correlation between laboratory tests and

weather resistance. He found a good correlation when the samples were boiled for 2½ hr. in 6% citric acid. To estimate the attack on enamels by acids and alkalis Roberts[76] uses an optical interference method to measure the thickness of the amorphous silica film formed on the surface of the enamel.

The question of adhesion does not now receive as much attention as it did a few years ago. Partridge,[77] however, has made some interesting comparisons between adhesion in glass–metal seals and adhesion of enamels, pointing out that the difference in the expansion coefficients is generally much greater in enamel–metal than in glass–metal even when the effect of iron oxide taken into solution by the enamel is allowed for. An investigation of the tendency of molten glass to adhere to heated metals[78] is of some interest to enamellers. The critical temperature at which beads of molten glass adhered when dropped on to an inclined metal surface were determined. The lowest adhesion temperatures were found for a Cr–Ni–W alloy (500° F.) and the highest (650° F.) for stainless steels. Adhesion to cast irons was generally found to occur at 600° ± 25° F.

Though it is known that a considerable amount of work is being carried out on ceramic coatings for the protection of metals in high temperature applications, comparatively little appears to have been published during the year. A number of coatings for molybdenum developed at the U.S. Bureau of Standards have, however, been described[79,80] including M–13–33 coating which consists of a base coat of low expansion frit containing 20% ZrO_2 followed by a cover coat containing 95% ZrO_2 and a sealing coat of the same composition as the base coat. It has been shown recently[81] that failure of coated heat-resisting alloys results primarily from interaction between the coating and oxide film formed on the metal. Complete coating is therefore necessary; exposed metal surfaces are to be avoided as attack will occur at the junction with the coated part and the coatings used should, if possible, be inert to the metal oxide. Several coatings for protection of metals at lower temperatures have also been devised, e.g. one which is claimed to protect metals up to 870° C. and to suppress infra-red radiation.[82]

Refractories

For some time now solid-phase relations in the high-MgO region of the system CaO–MgO–Al_2O_3–Fe_2O_3–SiO_2 have been fairly well understood and it has been possible to predict with fair precision the solid phases occurring under equilibrium conditions. Although this has thrown considerable light on the relation between chemical composition and refractory properties it has been evident that a fuller understanding could only come with a knowledge of the solid–liquid relationships in the appropriate regions of this system. To determine these fully is, however, a formidable task. Attempts to obtain the necessary information by methods sufficiently precise for technical purposes have been made by Rait[83] and more recently by Booth[84]; they are based on the visual determination of the melting behaviour of pellets chosen to produce certain combinations of phases known to coexist at equilibrium in the solid state. By varying the composition within a given phase-assemblage, eutectic

temperatures and compositions and liquidus temperatures within that particular assemblage can be determined with sufficient accuracy to enable liquid contents to be estimated for given temperatures and compositions. This method has been used by Rait, an account of whose work is now being published in a series of papers, four of which have appeared during the year. So far the known partial systems—binary, ternary and quaternary—have been discussed and new data on relevant portions of the systems $CaO–MgO–Fe_2O_3$, $MgO–Fe_2O_3–Al_2O_3$, $MgO–Fe_2O_3–SiO_2$ and $CaO–MgO–Fe_2O_3–SiO_2$ have been presented.

Booth, who has described his work in a paper to the British Ceramic Society, is concerned with the behaviour of magnesite and chrome–magnesite bricks and has adopted a somewhat simplified approach, e.g. in the case of magnesite bricks he neglects the contribution of free periclase to liquid formation, assuming melt formation to be due entirely to fusion of the minor phases which, with CaO/SiO_2 molecular ratios greater than two, all occur in the pseudo-ternary system spinel–forsterite–dicalcium silicate. The silicates forsterite, monticellite, merwinite and dicalcium silicate occur in pairs determined by the CaO/SiO_2 ratio. He has therefore studied the fusion relationships in this system for the cases where the spinel is $MgO.Al_2O_3$, $MgO.Fe_2O_3$ and mixed spinels of these two in various proportions. His diagrams show that replacement of Al_2O_3 in the spinel by Fe_2O_3 causes a marked increase in the range of compositions molten below 1400° C. and he has been able to show that a correlation exists between the temperature and amount of liquid formation and the refractoriness-under-load of magnesite and chrome–magnesite bricks.

In the field of applications an event of outstanding interest is the blowing-in of two blast furnaces with complete carbon linings; the decision to instal these linings was taken as a result of observations on the behaviour of trial panels. An interesting development in monolithic linings for high-frequency furnaces has been described.[85] By incorporating 4% sand with 2% borax into magnesite lining mixtures, expansions of the order of 1·5–2·0% have been obtained at 1150° C. apparently owing to the formation of a siliceous glass which reacts with the surface of the magnesite grains to form forsterite. This means that controlled expansions can be made to occur in the lining when in use, at some distance from the hot face; this restricts the formation of shrinkage cracks to a narrow zone at the working face and thus preserves steel-tightness. Magnesite linings incorporating these additions have now been in production for six years with considerable success. A similar principle may be involved in the apparently successful use in large high-frequency furnaces in Germany of olivene–magnesite mixtures designed to produce forsterite at working temperatures.[86] The properties of Norwegian olivene, which is finding increasing use as a refractory and for sand in steel foundries, have been described by Stenvick.[87] The marketing of this material is under the control of the Norwegian Government who are prepared to guarantee the quality.

Tests on silica bricks in torsion have been carried out by Das and Roberts[88] between room temperature and 1600° C. They find a marked fall in the elasticity modulus in the range of the α–β-cristobalite and

tridymite inversions, followed by a rapid rise which continues to about 1200° c. when it falls again. In this latter range and also in the range of the α-β changes irrecoverable deformation tending to a limit at a given load occurs, but the observed fall in the modulus was not due to this, as is shown by the slopes of the load–deformation curves obtained during removal of the load. Above 1500° c. continuous plastic flow sets in. The authors consider that the fall in the modulus in the inversion range may be due to a fall in the modulus of the crystals such as has been shown to occur with single crystals of quartz at 575° c. They also suggest that differential expansion between crystals and matrix may contribute to the observed increase above the transition range. These results again demonstrate the high load-bearing capacity of silica, since under the same conditions continuous flow was found to occur at 1200° c. in firebricks and at 1350° c. in chrome–magnesite. Cracking of silica products during manufacture has been investigated by Lynam and Nicholson[89] who reach the somewhat unorthodox conclusion that most of the cracking observed in fired bricks actually occurs during the drying operation, the cracks being revealed only after firing.

A study of coring in fireclay of the type used for making casting-pit refractories[90] has shown that the major factor determining coring is the change of texture that occurs when vitrification begins. Decreasing the vacuum during de-airing decreased the incidence of coring and diminished the volume of the closed pores after firing, the total porosity being practically unchanged. The spalling of firebricks has been discussed.[91] Resistance to spalling depends, it is suggested, on the ability to yield (or 'spall invisibly') at intergranular joints which must therefore be sufficiently weak to 'give.' High strength on the other hand depends on the development of strong joints. It is suggested that a brick containing only round, closed pores might fulfil the requirements of both strength and spalling resistance.

Various investigations into causes of failure of refractories are reported. Sosman and Patrick[92] have shown that Zn and ZnO can act as mild catalysts for carbon deposition in firebricks. Rigby[93] has described features he has observed in blast-furnace scaffolds. He suggests that the initial cause is oxidation of potassium cyanide to potash which reacts with the surface of the refractory to form a viscous slag containing potassium aluminosilicates such as leucite and kaliophilite. This produces a sticky surface to which the ore can adhere. Reduction of the ore by potassium cyanide vapour accounts for the sheets of metallic iron observed in such scaffolds. Other mechanisms apparently operate in some cases. The properties of iron cordierite from a blast-furnace hearth have been described.[94] The effect of a change-over to oil firing on the life of open-hearth refractories has been described by Marshall,[95] after 15 months' operational experience. In all the converted furnaces except one there was an improvement in roof life. There was also greater regularity of performance which enabled repairs to be forecast with greater certainty. Front- and back-wall performance was improved though there was a greater incidence of foaming slags. Gould[96] has described a method of assessing the effects of time, temperature and glass level on attack on glass-tank refractories. One effect of Fe_2O_3

in the glass is that it decreases attack below the surface owing to the production of steeper temperature gradients. The rate of oxidation of silicon carbide refractories has been shown to increase with decreasing particle size and to decrease with time because of formation of a coating of silica.[97] The presence of steam, however, seems to modify this layer in some way and causes a marked increase in the rate of oxidation.

A study of the factors affecting the failure of zircon refractories has shown that firing to 1650° c. or over causes a marked improvement in refractoriness-under-load and greatly reduces the effect of fluxing impurities.[98] This, it is considered, is due to the presence of zirconia (formed by partial decomposition of the zircon) in the siliceous glass phase, the viscosity of which is thus increased. The decomposition of zircon at high temperatures appears to start in cleavage planes of the crystal and as it is accompanied by an expansion it is thought to be responsible for the cleavages observed in the grains after certain heat treatments. A 'non-spalling' magnesite–chrome brick with, it is claimed, an unusually low modulus of rupture and a high deformation to rupture has been patented.[99] It is made from dead-burned magnesite with not less than 35% chrome and it contains no particles of intermediate size.

Considerable activity continues to be shown in the field of the 'special oxide' refractories. Investigations on BeO–SiO_2[20] and BeO–Al_2O_3[19] mixtures have already been mentioned. Studies of recrystallization at 2000° c. in bodies prepared by compacting powdered beryllia show that the relative increase in crystal size increases as the particle size decreases,[100] while shrinkage and bulk density also increase. It is concluded from this that there is a direct connexion between grain growth and sintering. This, however, is at variance with opinions generally held since, particularly in the field of powder metallurgy, it is considered that recrystallization (which takes place rapidly to a limiting size) is a 'transient' phenomenon having little effect on the progress of sintering as such. A study, using reflected light microscopy, of fracture at room temperature in test pieces of well-sintered alumina has shown that both trans- and inter-crystalline fracture occur; this indicates little difference in strength between the crystal grains and the grain boundaries.[101] Confirmation of this is found in the fact that the strength of a single crystal is of the same order as that of a polycrystalline bar. An investigation of bend strength and bend creep of high-temperature ceramics using a refined technique with four-point loading of the test-bars has also been described.[102] An interesting feature of the creep tests is the high creep rates observed with clear, fused silica at 1000° c. The factors controlling adherence in cermet bodies are being investigated.[103] It has been found that wetting of Al_2O_3 by metals is promoted by interaction of the Al_2O_3 with a layer of metal oxide, and it is suggested that sintering would be promoted by firing with limited oxidation or by using pre-oxidized metal particles. It is concluded that adhesion is most likely to develop when the metal oxide and the alumina have the same structure, so that solid solutions can form.

A useful paper on the slip casting of alumina has appeared recently and should prove of value to workers in this field.[104] Final deflocculation

is achieved either under acid conditions, or under basic conditions by the use of tetramethylammonium hydroxide.

Cements

In the production of Portland cement, clinker formation of $3CaO.SiO_2$ is of critical importance. A complicating factor affecting the ease of formation of this compound, however, is that its primary phase area in the system $CaO–Al_2O_3–SiO_2$ is of limited extent, and also that it melts incongruently giving lime as a stable phase in equilibrium with its melt. Hence its formation on cooling is apt to be inhibited by the development of coatings round unreacted lime crystals. In the system $CaO–4CaO.Fe_2O_3.Al_2O_3–3CaO.SiO_2$, on the other hand, $3CaO.SiO_2$ melts congruently forming a eutectic with CaO and it might therefore be expected that high Fe_2O_3 contents would favour increased and more rapid formation of $3CaO.SiO_2$. Tentative experiments along these lines by the present writer some time ago were, however, not particularly conclusive for the small laboratory mixes used, and they were not published. Recent published work[105] on Portland cement seems to indicate that the viscosity of the liquid phase at the sintering temperature is of primary importance to the progress of the reaction, low melt-viscosity favouring the formation of a high content of $3CaO{\cdot}SiO_2$ and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$, and low unreacted lime in the melt. The saturation concentration of MgO in the melt, on the other hand, shows a definite relation with the Fe_2O_3 content, the MgO content being 4·35% in a normal mix and 11·3% in a mix to which Fe_2O_3 had been added.

It is now fairly certain that the compound $5CaO.3Al_2O_3$ identified by Rankin and Wright in the system $CaO–Al_2O_3$ was in reality $12CaO.7Al_2O_3$. In the crystallization of high-alumina cements what may be an unstable modification of this compound often appears. Experiments at the Building Research Station, in which $CaO–Al_2O_3$ glasses were annealed at various temperatures, gave this unstable compound only at temperatures below 1020° c. and Lea and Nurse[12] suggest two possibilities: (i) that the observed compound is a low-temperature modification of '$5CaO.3Al_2O_3$' or (ii) that below 1020° c. '$5CaO.3Al_2O_3$' decomposes to give $CaO.Al_2O_3$ and $2CaO.Al_2O_3$. As against either of these suggestions, systems in which the liquidus falls below 1020° c. deposit normal '$5CaO.3Al_2O_3$,' though it is possible that this may be due to an alteration in the transformation temperature due to solid solution. Another explanation may be that such phases represent truly metastable 'structure phases' of the type found to separate from certain glasses. Such a postulate would go far to explain the many unusual phases proposed from time to time by workers on cements.

An investigation of cements made by fusing mixtures of alumina, $CaCO_3$ and silica is reported[106]; the Al_2O_3 contents of the final cements varies from 55–70% and the SiO_3 contents from 2–8%; the refractoriness varied from 1400–1700° c., rising with increasing Al_2O_3 content, and with increasing SiO_2 content for Al_2O_3 contents of 60% and over. In concretes prepared from these cements with a variety of fillers the temperatures of subsidence were in general 70–100° c. higher than with normal aluminous cement using the same fillers.

A method of increasing clinker adhesion in rotary cement kilns by blowing bauxite, iron ore, roasted pyrites, etc., through the coal-dust nozzle has been described.[107] The efficiency of this operation can be gauged by taking temperature readings on the shell by means of a contact pyrometer. A method of producing light-weight aggregate for low-density concretes has been patented.[108] A 'bloating' clay, after breaking up, is passed through an initial heating zone for a sufficient time to heat it uniformly to a temperature just below the bloating temperature. It is then heated to the bloating temperature. The object of the pre-treatment is to prevent the particles cohering to form large lumps. To prevent the absorption of excessive moisture by light-weight aggregate during mixing the aggregate is first dusted with an alkali-salt of the petroleum-hydrocarbon-insoluble portion of pine-wood resin.[109] This salt, on the surface of the aggregate, undergoes slow conversion to an insoluble salt of a heavy metal ion of the cement and thus forms a waterproof film. This treatment is suitable for use with expanded vermiculite.

An investigation of the rate of hydration of Portland cements and their components[110] indicated that the order of decreasing hydration rate in first stages was $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, $3CaO.SiO_2$ and $2CaO.SiO_2$, the last being very slow. After six months the degree of hydration of the first three tended to become equal. The compounds formed were $3CaO.Al_2O_3.6H_2O$ from $3CaO.Al_2O_3$; $3CaO.Al_2O_3.6H_2O$ and $CaO.Fe_2O_3.H_2O$ from $4CaO.Al_2O_3.Fe_2O_3$; $2CaO.SiO_2.H_2O$ and $Ca(OH)_2$ from $3CaO.SiO_2$; and $2CaO.SiO_2.H_2O$ from $2CaO.SiO_2$. The hydration of Portland cement was faster than that of its constituents. A proposed retarder for the setting of cements is an addition of 0·03–0·07% by weight of cellulose oxidized by contact with NO_2, and inorganic salts of cellulose oxidized in this way.[111] To retard setting and give a uniform rate of setting over the range 140–200° F. a suitable adjusted mixture of maleic acid and a modified starch is proposed.[112]

A method of producing expansions in cements which has been patented[113] is to add a mixture of aluminium hydroxide, calcium hydroxide and gypsum, which form calcium sulpho-aluminate during setting. In discussing the mechanism of expansile changes in cements Lea and Nurse[12] state that the degree of expansion accompanying the hydration of plaster of Paris depends on the crystal habit assumed by the gypsum formed. With water as the medium the crystals grow in an acicular form and a high expansion results, whereas the presence of additions which give more isometric forms results in a smaller expansion. The expansile forces developed in such cases are usually low. They also quote the action of $CaSO_4$ solutions on the hydrated alumina compounds of set Portland cement, which results in the formation of elongated, hexagonal needles of $3CaO.Al_2O_3.3CaSO_4.22H_2O$, which causes an outward thrust that disrupts the solid mass. The present writer is in agreement with the view that directional growth of crystals can cause over-all expansions of this kind even when no appreciable change in specific volume is involved and he has held the view for some time that the expansions occurring in certain clays when mullite is forming are due to this cause.[114]

The use of soluble silicates as bonds in refractory and acid-resisting

cements has been discussed by Glass.[115] He points out that a disadvantage associated with the use of sodium fluoride as an accelerator is that exposure to strong acid tends to weaken the bond between brick and mortar, possibly owing to generation of HF. For this reason organic reagents which hydrolyse to give acids are sometimes preferred, e.g. ethyl acetate.

Analytical and physical measurements

It is well known that test data, even when determined by specified methods, may be misleading. It is generally left to the enthusiast to apply the yard-stick of statistical analysis to demonstrate the consequence of living in an imperfect world where errors accumulate or cancel out according to the workings of the laws of chance. A considerable debt is, therefore, owed to Cross and Young for their efforts in this direction over the past few years. In a recent paper[116] they follow up their work on the 'hot test-piece–boiling water' (H.T.B.W.) method of determining apparent porosity and bulk density[117] with an investigation of the accuracy of apparent solid density determinations on silica bricks, as compared with solid density determinations using the Rees–Hugill flasks. Their results show that the A.S.D. (apparent solid density) determination is the more accurate, and for normal silica bricks the value obtained differs to a negligable extent from the solid density; this is because the volume of the closed pores is on the average small and because the liability to variation due to closed pores is less than the uncertainty in the Rees–Hugill method as normally carried out. The crux of the matter is that where very large numbers of determinations have to be carried out the H.T.B.W. method offers an appreciable saving in time. It will be noted that a new system of nomenclature is used by those authors for the various degrees of density of porous materials, the terms bulk density (mass/bulk volume), apparent solid density (mass/apparent solid volume) and solid density (mass/solid volume) being proposed to avoid the ambiguities of the present system. The same authors have also described a gas-fired laboratory furnace which permits the simultaneous heating of 54 test-pieces at temperatures up to 1600° C. with a temperature-spread within $\pm 5°$ C.[118] They intend to use this to study variability in the permanent linear-change test and their results will be awaited with some interest.

A French committee has recently completed a general survey of methods of testing,[119] five laboratories collaborating in carrying out the tests. Their findings are illuminating, the accuracy of the various test figures being as follows: chemical analysis (30–35% Al_2O_3 firebrick): SiO_2 $\pm 3\%$; Al_2O_3 $\pm$ 2%; Fe_2O_3 $\pm$ 1·2%; TiO_2, CaO, MgO, alkalis $\pm$0·4%; refractoriness $\pm$1 cone; bulk density $\pm$0·02 g./c.c.; cold crushing strength $\pm$15%; after contraction $\pm$1% at 1500° C.

The inaccuracy of the indirect determination of alumina by difference has long been realized and various direct methods have been suggested, of which the 8-hydroxyquinoline method has received the most attention. A report just issued describes its use for the determination of alumina in high-silica materials.[120] It is not recommended, however, for materials giving more than 10% residue after HF treatment. A polarographic

method for the determination of alumina in Portland cement has also been described.[121] and progress is apparently being made in developing spectrographic techniques of improved accuracy.[122,123] Greater accuracy in the separation of CaO as oxalate is claimed to result by utilizing the hydrolysis of urea to raise the p_H of a solution containing the Ca and oxalate ions[124] and an improved method for the determination of alkalis is reported.[125] A rapid method for the determination of nickel on the surface of enamelling iron has also been described.[126]

In the U.S. the Geiger-counter X-ray spectrometer is finding increasing use in the field of ceramics and has been used to determine the relative proportions of cubic and monoclinic ZrO_2 in heat-treated zirconia bodies[127]; in a discussion[128] some criticisms were made of the fact that the accuracy claimed by the authors was based on a somewhat nebulous estimate. An improved type of mount for powdered specimens, intended to give a high degree of random orientation and improved uniformity, has been described.[129]

A new approach to the permeability method for specific surface has been made by Svensson[130] who, in contradiction to Rigden, assumes that molecular flow is always fully developed when gases flow through a porous bed. He also assumes that the length of the capillaries is proportional not to the length of the bed but to the length filled (on the average) by particles, which is in turn related to the porosity. A critical discussion of the various methods of determining surface area has been published by Blake.[131]

A replica technique for the quantitative measurement of surface finish of enamels has been described,[132] based on the measurement of haze, i.e. the light lost by scattering when a beam is passed through the replica. An optical method has also been used to study adhesion of enamels, reflectance being measured from the area damaged by a standard impact.[133]

References

1 Rigby, G. R., *Trans. Brit. ceram. Soc.*, 1949, **48**, 1
2 Chesters, J. H., Howes, R. D., Halliday, M. D. and Philip, A. R., *J. Iron Steel Inst.*, 1949, **162**, 385
3 Howes, R. and Philip, A. R., ibid., 385
4 Halliday, I. M. D. and Philip, A. R., ibid., 401
5 Newby, N. P., ibid., 452
6 Houwink, R., Proceedings of the International Congress of Rheology, 1948. Parts I and III. (Amsterdam : North Holland Publishing Co., 1949)
7 Goodeve, C. F., *ibid.*, Parts II and V
8 de Waele, A. and Mardles, E. W. J., *ibid.*, Part II, 166
9 Barrer, R. M., 'Crystal Growth,' *Discuss. Faraday Soc.*, 1949, No. 5, 326
10 van Praagh, G., ibid., 338
11 Thomas, L. A., Wooster, N. and Wooster, W. A., ibid., 348
12 Lea, F. M. and Nurse, R. W., ibid., 345
13 Colegrave, E. B., Richardson, H. M. and Rigby, G. R., ibid., 352
14 Hall, F. P. and Insley, H., Supplement No. 1, *J. Amer. ceram. Soc.*, 1949, **32**, Dec., Part 2
15 Darken, L. S. and Gurry, R. W., *J. Amer. chem. Soc.*, 1946, **68**, 799
16 White, J., *J. Iron Steel Inst.*, 1943, **148**, 579
17 Idem, ibid., 1949, **163**, 151
18 Levin, E. M. and McMurdie, H. F., *J. Amer. ceram. Soc.*, 1949, **32**, 99
19 Foster, W. F. and Royal, H. F., ibid., 26

[20] Morgan, R. A. and Hummel, F. A., ibid., 250
[21] Riddle, F. H., ibid., 333
[22] Ford, W. F. and Rees, W. J., *Trans. Brit. ceram. Soc.*, 1948, **47**, 207
[23] Idem, ibid., 1949, **48**, 291
[24] Ford, W. F. and White, J., ibid., 417
[25] Goldsmith, J. R., *Amer. Min.*, 1949, **34**, 471
[26] Coughanour, L. W. and Norton, F. H., *J. Amer. ceram. Soc.*, 1949, **32**, 129
[27] Schofield, R. K., *Trans. Brit. ceram. Soc.*, 1949, **48**, 207
[28] Johnson, A. L., *J. Amer. ceram. Soc.*, 1949, **32**, 210
[29] Perkins, A. T., *Soil Sci.*, 1949, **67**, 41
[30] Barshad, I., *Amer. Min.*, 1949, **34**, 675
[31] Roy, R., *J. Amer. ceram. Soc.*, 1949, **32**, 202
[32] Gad, G. M. and Barrett, L. R., *Trans. Brit. ceram. Soc.*, 1949, **48**, 352
[33] Towers, H., ibid., 371
[34] Gruver, R. M., Henry, E. C. and Heystek, H., *Amer. Min.*, 1949, **34**, 869
[35] Murray, P. and White, J., *Trans. Brit. ceram. Soc.*, 1949, **48**, 187
[36] Grimshaw, R. W., Westerman, A. and Roberts, A. L., ibid., 1948, **47**, 269
[37] Plumat, E., *Verre et Silicates ind.*, 1948, **13**, No. 6, C.O.B.E.A. Suppl. 81
[38] Schulman, J. H., Claffy, E. W. and Gunther, R. J., *Amer. Min.*, 1949, **34**, 869
[39] Beck, W. P., *J. Amer. ceram. Soc.*, 1949, **32**, 147
[40] Hummel, F. A., ibid., 320
[41] Rosenthal, E., 'Pottery and Ceramics,' Pelican Book A 201 (Harmondsworth: Penguin Books, 1949)
[42] Johnson, A. L., Postlethwaite, D. E. and Rittenberg, S. C., *J. Amer. ceram. Soc.*, 1949, **32**, 347
[43] Russell, R., Mohr, W. C. and Rice, H. H., ibid., 105
[44] Lamar, R. S., ibid., 65
[45] Gebler, K. A. and Wisely, H. R., ibid., 163
[46] Hursh, R. K., ibid., 75
[47] Tuttle, N. A. and Cook, R. L., ibid., 279
[48] Baldwin, W. J., *Ceramic Age*, 1949, **53**, 188
[49] Wainer, E. (National Lead Co.), U.S.P. 2,467,169
[50] Titanium Alloy Manuf. Co., B.P. 619,538
[51] Bunting, E. N., Shelton, G. R. and Creamer, A. S., *J. Res. nat. Bur. Stand.*, 1949, **43**, 237
[52] Ryder, S. H., *Trans. Brit. ceram. Soc.*, 1949, **48**, 375
[53] Luttrell, C. B., *J. Amer. ceram. Soc.*, 1949, **32**, 327
[54] Cook, R. L. and Brunner, C. D., ibid., 401
[55] *Pott. Gazz.*, 1949, **74**, 142
[56] *Times Rev. Industr.*, 1949, **3**, No. 26, 47
[57] Hetherington, A. L., *Nature*, 1949, **163**, 900
[58] Smith, A. N., *Trans. Brit. ceram. Soc.*, 1949, **48**, 85
[59] Shartris, L. and Canga, R., *J. Res. nat. Bur. Stand.*, 1949, **43**, 221
[60] Dietzel, A., *Mitt. dent. Ker. Ges.*, 1949, No. 1, 12; No. 2, 15
[61] Millar, N. S. C., *Foundry Tr. J.*, 1949, **87**, 727
[62] Marbaker, E. E., Saunders, H. S. and Baumer, L. N., *J. Amer. ceram. Soc.*, 1949, **32**, 197
[63] Cook, R. L. and Essenpries, J. F., ibid., 114
[64] Huppert, P. A., *Finish*, 1948, **5**, 19
[65] Coffeen, W. W., *J. Amer. ceram. Soc.*, 1949, **32**, 10
[66] Carlisle, P. J., Deyoup, A. J. and Short, A. O., *Finish*, 1949, **6** (1), 42; (2), 33
[67] *Ceramics*, 1949, June, 201
[68] Shands, E. H., *Finish*, 1948, **5**, 25
[69] Lannan, J. L., *Proc. Porcelain Enamellers Inst. Forum*, 10th Forum, 1948, 27
[70] Porter, F. R., *J. Canad. ceram. Soc.*, 1948, **18**, 30
[71] King, B. W. and Stull, C. W., *J. Amer. ceram. Soc.*, 1949, **32**, 34
[72] Bruce, B. D. and Sharon, A. V., ibid., 41
[73] Harrison, W. N. and Moore, D. G., ibid., 15
[74] Idem, *J. Res. nat. Bur. Stand.*, 1942, **28**, 735
[75] Sweo, B. J., *J. Amer. ceram. Soc.*, 1949, **32**, 356
[76] Roberts, J. T., ibid., 243
[77] Partridge, J. H., *Sheet Metal Industr.*, 1948, **25**, 2225

[78] Kapnicky, J. A., Fairbands, H. V. and Koehler, W. A., *J. Amer. ceram. Soc.*, 1949, **32**, 305
[79] Moore, D. G., Laby, L. H. and Harrison, W. N., National Advisory Committee on Aeronautics, Technical Note No. 1626, 1948
[80] *Steel*, 1949, **124**, No. 4, 59, 82
[81] Moore, D. G., Richmond, J. C. Harrison, W. N., National Advisory Committee on Aeronautics, Technical Note No. 1731, 1948
[82] Bennett, D. G. and Andrews, C. M., U.S.P. 2,475,470
[83] Rait, J. R., *Iron & Steel*, 1949, **22**, 187, 289, 493, 623
[84] Booth, C., *Trans. Brit. ceram. Soc.* (in press).
[85] Chesters, J. H., Lea, E. C. and Mackenzie, J., ibid., 1949, **48**, 263
[86] Stutzel, H., *Stahl u. Eisen*, 1949, **69**, 403
[87] Stenvick, K. J., *J. Iron Steel Inst.*, 1949, **161**, 44
[88] Das, S. and Roberts, A. L., *Trans. Brit. ceram. Soc.*, 1949, 48
[89] Lynam, T. R. and Nicholson, A., ibid. (in press); also *Ceramics*, 1949, Nov., 503
[90] Cowling, K. W. and Elliott, K., *Trans. Brit. ceram. Soc.*, 1949, **48**, 123
[91] Moore, C. E., ibid., 176
[92] Patrick, R. F. and Sosman, R. B., *J. Amer. ceram. Soc.*, 1949, **32**, 133
[93] Rigby, G. R., *J. Iron Steel Inst.*, 1949, **161**, 295
[94] Richardson, H. M. and Rigby, G. R., *Miner. Mag.*, 1949, **28**, 547
[95] Marshall, D. F., *J. Iron Steel Inst.*, 1949, **161**, 301
[96] Gould, C. E., *J. Soc. Glass Tech.*, 1949, **33**, 5T
[97] Lea, A. C., ibid., 1949, **33**, 27T
[98] Stott, V. H. and Hilliard, A., *Trans. Brit. ceram. Soc.*, 1949, **48**, 133; Hilliard, A. and Stott, V. H., ibid., 143
[99] Huer, R. P. (General Refractories Co.), U.S.P. 2,443,424
[100] Duwez, P., Odell, F. and Taylor, J. L., *J. Amer. ceram. Soc.*, 1949, **32**, 1
[101] Roberts, J. P., *Proc. phys. Soc.*, 1949, **62**, 248
[102] Roberts, J. P. and Watts, W., *Trans. Brit. ceram. Soc.*, 1949, **48**, 343
[103] Blackburn, A. R., Shevlin, T. S. and Lowers, H. R., *J. Amer. ceram. Soc.*, 1949, **32**, 81
[104] Hauth, W. E. Junr., ibid., 394
[105] Berg, V. and Bohler, A. G., *Radex Rundsch.*, 1949, No. 1, 4
[106] Kukolev, G. V. and Roizen, A. I., *Ogneupory*, 1948, **14** [2], 65
[107] Anon., *Radex Rundsch.*, 1949, No. 3, 112
[108] Ryner, A., B.P. 619,888
[109] Watts, V. E. (Materials Engineering Corpn.), U.S.P. 2,463,927
[110] Butt, Y. M., *J. appl. Chem., USSR*, 1949, **22** [3], 223
[111] Ludwig, N. C. (Universal Atlas Cement Co.), U.S.P. 2,471,632
[112] Idem, U.S.P. 2,470,505
[113] Schenker, F. A. and Shann, T. A. (Kasper Winkler & Co.), U.S.P. 2,465,278
[114] White, J., *Trans. Brit. ceram. Soc.*, 1948, **47**, 389
[115] Glass, H. M., ibid., 1949, **48**, 161
[116] Cross, A. H. B. and Young, P. F., ibid, 99
[117] Idem, ibid., 1948, **47**, 121
[118] Idem, ibid. (in press); also *Ceramics*, 1949, Nov., 499
[119] Letort, Y., *Bull. Franç. Ceram.*, 1949, No. 2, 31
[120] British Ceramic Research Association, Special Publication No. 2, 1949
[121] Ford, C. L. and LeMar, L., *Bull. Amer. Soc. Test. Mat.*, 1949, No. 157, 66
[122] Herdle, A. J. and Wolthorn, W. J., *Analyt. Chem.*, 1949, **21**, 105
[123] Steinberg, R. H. and Belic, H. J., ibid., 730
[124] Inglis, R. S. and Murray, P. E., ibid., 525
[125] Elving, P. J. and Chao, P. C., ibid., 507
[126] Ikenberry, L. C. and Canfield, J. J., *J. Amer. ceram. Soc.*, 1949, **32**, 308
[127] Duwez, P. and Odell, F., ibid., 180
[128] Ibid., 184
[129] McCreery, G. L., ibid., 180
[130] Svensson, J., *Jerukontorets Ann.*, 1949, **133** [2], 33
[131] Blake, P. D., *J. Soc. chem. Ind.*, 1949, **68**, 138
[132] Richmond, J. C. and Francisco, A. C., *J. Amer. ceram. Soc.*, **1949, 32, 170**
[133] McLaughlin, J. L., ibid., 166

GLASS

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THE output of literature relating to the science and technology of glass increases continually, and this review does not claim to cover more than a selection from the publications of the past year.

The constitution of vitreous systems has again been dealt with in a considerable number of papers which include the majority of those read at the meeting of the International Commission on Glass held at Buxton during October, 1948. Certain of these papers are necessarily of an exploratory character because of lack of experimental evidence, as some of the authors have themselves pointed out.

A gratifying occurrence has been the reappearance of three German periodicals devoted to glass and allied subjects. *Glastechnische Berichte*, which has been in abeyance since 1943, recommenced publication in August, 1948, and continues to enrich glass technology with many high-quality papers. Other reappearances were *Die Glashütte* (April 1948) and *Sprechsaal* (October 1949).

The constitution of vitreous systems

The contributions to the symposium on the 'Nature and Constitution of Glass' read at the meeting of the International Commission on Glass included a paper by S. M. Cox,[1] who assumed that the distribution function associated with the randomness of the Si–O ionic spacings in glass is approximated by a two-cell histogram, and on this assumption derived approximate formulae for the thermal, viscous, and elastic properties of silica-rich glasses.

W. A. Weyl[2] contributed to the symposium a paper on the surface properties of glasses as affected by heavy metal ions, and pointed out that, although the relatively simple laws of crystal chemistry as applied by Zachariasen and Warren have been satisfactory for interpreting the structure of most glasses, they are not applicable to glasses containing large ions such as Ba^{2+} or ions having an electronic structure that differs from that of the inert-gas atoms (Zn^{2+}, Cd^{2+}, Pb^{2+}), the outer electron shell of which is distorted in an electrical field to give an asymmetrical structure. From the nature of these distorted ions, it was to be expected that their presence would have greater effects on the surface properties of glasses than on their bulk properties. The author claimed that a number of properties could be explained on the basis of a chemical picture of the distorted lead ion, e.g. that some glasses containing lead oxide have a positive temperature coefficient of surface tension, and that the presence of Pb^{+2} or similar ions provides a bridge between the structures of glasses and of noble metals.

The lack of any satisfactory fundamental explanation of the variation of viscosity of a glass with temperature has again stimulated a certain number of theoretical papers dealing with viscosity and the flow or deformation of glass at both high and low temperatures. Reference has already been made to the paper by S. M. Cox. In addition to this, there are two

useful papers by G. O. Jones. In the first of these,[3] the fundamental theory of the liquid and glassy states is briefly reviewed, and a number of experiments on glasses are suggested. The paper deals with phenomena in the transformation region, the kinetics of the stabilization process, melting, crystallization and homogeneity, mechanical and electrical 'flow' properties, Griffith flaws, permeability of glasses to He, H. etc., and theoretical calculation of bond energies; consideration is given also to the entropy of supercooled liquids at 0° K.

In his second paper,[4] G. O. Jones reviews and discusses experimental data on the flow of glass of very high viscosity, i.e. at temperatures below the transformation region, from the standpoint of modern rheological theory, with special reference to the form of the function governing the delayed elastic effect and the variation of the total magnitude of this effect with the temperature.

R. W. Douglas[5] has derived and discussed the full expression for the coefficient of viscosity and examined this in the light of published data. In general, satisfactory agreement between theory and practical results is obtained, but particularly at the lower temperatures there is a need for elaboration of the theory. It is emphasized that the available data is scanty for checking theoretical predictions, and that the agreements obtained do no more than indicate that the theory is not incompatible with the observations. In a more general paper, A. H. M. Andreasen[6] puts forward model laws concerning the relation of viscosity forces and gravitational forces and of viscosity forces and surface forces; he expresses the view that the validity of these two laws can be counted upon when other kinds of force, e.g. inertia forces, can be neglected, and that this will be applicable generally to systems of highly viscous liquids.

In a joint paper, R. W. Douglas and G. O. Jones[7] have supplemented previous work on a theoretical attempt to interpret the physical properties of glasses in terms of the atomic arrangements revealed by X-ray diffraction, by describing changes of density with time in the transformation range in vitreous silica, a borosilicate glass, and a soda–lime–silica glass, in the light of the analogy between the atomic structure of glasses and liquids. J. E. Stanworth[8] presented arguments in favour of regarding glasses as collections of ions arranged in space in a manner having general similarity to that observed in crystals though with characteristic differences.

In opening the discussion on some of the papers read for the symposium, Adolf G. Smekal[9] gave a résumé of work done in recent years in Germany with special reference to the relations between the mechanical strength and structure of glass.

H. A. Sheybany,[10] in an interesting series of papers, has studied the mode of filling cavities in the glass networks with ions, and the effect of ionic field intensity on the structure of glasses of the systems Li_2O–Na_2O–SiO_2; Li_2O–K_2O–SiO_2 and K_2O–Na_2O–SiO_2.

W. A. Weyl[11] has shown by schematic representation of the distribution of bond strength in ideal and real crystals, in glasses, and in surface films, the similarity between the surfaces of crystals and the structure of glasses, and on this picture has explained a number of apparently unrelated phenomena. R. Fricke[12] has studied amorphous conditions and lattice

breakdown in crystals and their relation to glass manufacture, whereas H. O'Daniel[13] has discussed the structure of silicate glasses on the basis of information gained by the use of X-rays in conjunction with a study of crystal chemistry.

The principles of the Raman spectrum and the methods of producing and evaluating it, together with a brief review of Raman investigations carried out by various workers on different types of glass, have been given by G. Ruess,[14] whose work has been critically examined by A. Smekal.[15]

Radioactive tracers have been used in studying glass structure. H. H. Blau and J. R. Johnson,[16] using the diffusion of ^{24}Na between 550° and 750° C. and a newly developed photographic technique, found that values of the 'diffusion constant' D were reproducible to within less than 3%. They affirm that this work has progressed far enough to demonstrate that true fundamental values of energy of activation are being made available. F. L. Jones and N. J. Kreidl[17] have discussed the optical properties of glass in relation to its constitution, and W. A. Weyl [18] has attempted to correlate the dielectric properties of glass with its structure. As a contribution to the experimental study of structural changes in glass, J. Gillod[19] has given a new interpretation of expansion curves from which he deduces conclusions regarding annealing temperatures.

F. A. Hummel[20] has studied the properties of some substances isostructural with silica and reports that aluminium orthophosphate ($AlPO_4$) is more closely related structurally to SiO_2 than to any other natural or artificial mineral yet obtained ; also, that the thermal expansion behaviour of the cristobalite type of $AlPO_4$ is so similar to that of cristobalite that a high temperature structural relationship obviously exists.

Glass-making materials and compositions

The production of sands of satisfactory purity from contaminated sands and sandstones continues to receive attention at intervals, though the value of any process that may be developed must be assessed on economic as well as on scientific considerations. Two papers on this subject have been published during the year: J. P. Poole[21] describes a technique of attrition grinding which makes possible the production of a high-quality sand for the manufacture of white glass from a low-grade sandstone ; in the other paper E. C. Sawyer[22] puts forward a method of refining silica sand for glassmaking by flotation, acid treatment, steaming and washing, and finally drying and screening. This results in a sand containing less than 0·01% of iron oxide and a negligible quantity of alumina.

The publication of experimental work leading to results that have been well known in this country for many years, and that have been long accepted in practice, is a somewhat startling revelation of the extent to which different countries have followed their own lines of development in certain directions. It is rather surprising, e.g., to come upon papers relating to the use of sodium sulphate in glass batches and the relative merits of 'heavy ash' and 'light ash' as in the following examples.

R. Glowka and O. Strange[23] have contributed to a discussion on the use of sodium sulphate in glass melting and technical improvements resulting from the substitution of sulphate for some of the soda ash in glass batches,

and related problems. The reactions which occur during the melting of glass batches containing sulphate are also dealt with in a paper by M. Plumat,[24] who points out that the series of reactions begins with the formation of sodium sulphide, not sodium sulphite as has been commonly accepted. This is in accordance with the results obtained some years ago by A. Sherlock and described by him in a paper which unfortunately was not published owing to his premature death. The use of soda and its substitutes in glass melting has been discussed in some detail by H. Jebsen-Marwedel,[25] who points out that the 'heavy, granular soda' is more suitable than the 'light soda' (fine-grained), which is more liable to be carried away by the furnace gases and to cause partial or total blocking of the flues and regenerators. This is in accordance with experience in this country and America, where 'heavy ash' has been used almost universally for many years. Substitutes for soda have also been discussed by A. Dietzel.[26]

The literature on the boiling point of sodium sulphate has been reviewed by N. Quaiser[27] who explains the widely differing statements concerning the violence or turbulence of its boiling at temperatures above 1450°c. by the chemical reaction taking place when Na_2SO_4 is in contact with free silica. L. Stuckert and F.-J. Rauter[28] have reported that sodium sulphate liquor, remaining after the treatment of clay with NaOH to produce artificial bauxite, is entirely free from iron and when precipitated with $TiCl_4$ gives an iron-free titanium silicate which can be used to produce completely colourless, high-titania glasses; A. W. Schmidt[29] has also discussed the production of high-titanium colourless glasses.

The use of zircon or zirconia in glass has been referred to briefly by S. J. Johnston[30] and also anonymously.[31] The Na_2O–BeO–B_2O_3 system has been studied by H. Menzel and J. Adam,[32] and the ternary and quaternary systems alkali oxide–CaO–SiO_2–CO_2 by C. Kröger[33]; K. H. Sun[34] has discussed aluminate glasses.

Glass melting

Appropriately, the first paper to appear in the recently republished *Glastechnische Berichte* is a continuation from the last issue to be published before this periodical ceased to appear in 1943. This is Part II of H. Jebsen-Marwedel's study of the mechanism of glass fusion,[35] and it is devoted to a discussion of the movements that can be caused by surface tension. The author shows that even such slight chemical changes in the surface of the glass as are caused by a reducing atmosphere in the furnace or by working in a blowpipe may lead to internal stresses sufficiently great to cause cracking. He also states that, in a glass melt, a constituent which has a low surface tension will flow round the particle boundaries of the other components and form cords of different composition. In another paper on this subject, H. Jebsen-Marwedel[36] likens the influence of surface tension and capillarity, or the tendency to cord formation, to the splitting of unicellular organisms; in yet another paper, H. Jebsen-Marwedel[37] offers an analogy in the behaviour of soap solutions.

Problems of heat transfer in the melting of glass are of special importance from the production standpoint, and although much attention has

been paid to these problems, there is not yet unanimity of opinion on the relative importance of heat transfer by conduction, convection and radiation, nor of the part played by absorption in and re-radiation from those portions of the glass that are at intermediate temperatures. The extent to which these problems are still receiving attention is indicated by the five papers summarized below.

Heat transfer by radiation in heated glass has been reported on by V. V. Rodnikova[38] who cooled coloured and colourless glasses by conduction and radiation. The investigation of heat flow in the glass industry and in the ceramic industry by means of an electric analogy has been described by V. Paschkis, [39] also E. Bonnier.[40] A translation of a Russian paper on the role of radiation in the transmission of heat in glass has been published[41]; K. Dunn[42] has also discussed this subject. Heat transfer by radiation to surfaces at low temperatures has been studied by M. Blackman[43] and co-workers, who refer to silvered glass in this connexion.

A novel method of studying the melting of glass batches by means of radioactive tracers has been described by S. Lindroth,[44] who used this means to measure the rate of decrease in grain surface, which was taken as an index of rate of melting. Batch samples were treated with radiothorium nitrate solution, and subsequently sieved and heated at 10° per minute to 900–1000° c. The release of the emanation atoms as a function of temperature was measured by their ionizing effect on a current of nitrogen passing through the sample into an ionization chamber connected to an amplifier and a sensitive galvanometer. The course of the emanation curve for a base glass of composition Na_2O, 16%, CaO, 10%, SiO_2, 74%, caused by the addition of small amounts of minor constituents, was studied as well as the deviations. The values obtained were in fair agreement with results from direct observation of the decrease in height of cones made from the batches.

M. Lepingle[45] has discussed the temperature of fusion of various binary systems incorporating silica. H. M. Bateson[46] has described and discussed problems concerning the melting of glasses containing various proportions of lead in tank furnaces. C. Kröger[47] has discussed the equilibrium, speed of reaction, and relationship to the glass melting process of the ternary and quaternary systems: alkali oxide–CaO–SiO_2–CO_2. The evolution of sulphur compounds of sodium during fusion of glass has been discussed by M. Plumat.[48]

C. A. Faick and co-workers[49] have established the role of convection currents as a cause of striae distribution in pot melts of borosilicate glass; M. Quadrelli[50] has discussed currents in tank furnaces. The causes of 'cord' and bubble have also been the subject of study by various workers, as described in the group of papers referred to below.

The effects, measured by seed count, visual analysis, and low-temperature viscosity, of the major and some minor constituents on the melting and fining characteristics of amber and of white container glasses have been dealt with in a paper by D. P. Enright and co-workers.[51] A Dietzel,[52] in a study of gases in glass, has pointed out that the problem of the solubility of gases in glass melts during the fining process is partly a physical question and partly one of chemical gas reactions. A novel suggestion to explain the formation of gas bubbles in glass has been put

forward by P. Beyersdorfer and F. Jockmann,[53] who assert that the use of cullet containing arsenic, together with a glass batch containing salt-cake, is detrimental because of the persistent formation of gas bubbles at 1300° c. Direct correlation of systematic changes in the composition of a glass with its gas permeability has been presented by T. F. Newkirk and F. V. Tooley,[54] who studied the effect in the alkali–silica glasses.

Electric melting has again been the subject of important publications. The principles underlying the electric melting of glass have been dealt with in considerable detail by Ivan Peyches.[55] He points out that calculation of the resistance or conductivity of the glass in a tank, between electrodes in specified positions, is too involved to be practicable, owing to the wide variations of temperature from point to point and to the chemical heterogeneity of the glass. Measurements were therefore made of the electrical characteristics of an experimental tank, and from these were derived the resistivity of the homogeneous medium that would give the same characteristics. The effects of the shapes and positions of the electrodes and of the shape of the tank on the 'current-lines' and on the heat distribution in the tank are considered with reference to the design of furnaces with transverse, longitudinal or Y-shaped current flow. The uses of additional electrodes for giving local high current densities and concentrated generation of heat, for creating or baffling glass currents, are also dealt with. The application of these principles to the design of furnaces heated by electricity alone and by electricity and gas are illustrated by reference to various commercial tank furnaces. E. Meigh[56] has also discussed the electric melting of glass with particular reference to the French practice of combining electric heating with normal flame heating, and electric melting generally has been discussed anonymously.[57]

G. E. Howard[58] has entered a plea for a fundamental revision of furnace design and a departure from the continuous tank in favour of a low-temperature pretreatment of a briquetted batch, utilizing the heat of the waste gases and using the tank only for high temperature melting and fining processes.

Furnaces, refractories and fuels

The increasing need for the utmost economy in fuel consumption in glass furnaces has made it desirable to obtain more precise information concerning the heat input and the amounts of heat lost from the furnace in various ways. Accurate measurement of heat input is obviously the first stage necessary to the obtaining of such information, and a report of the Furnace Committee of the Society of Glass Technology has been published,[59] dealing with the measurement of heat input by the precise measurement of the quantity of fuel used and its calorific value. Types of gas meters for clean gas are listed, and methods for measurement of hot raw producer gas are discussed, including brick and steel-plate orifices and a venturi meter which is said to be less susceptible to errors when used in unfavourable locations. Various makers of meters for the flow of liquid fuels are listed, with notes on the experience with a number of these meters in this country. Notes on sources of information relating to the determination of calorific value are also given.

The fundamental technical and thermal principles of furnace construction and of firing methods with different fuels, with particular reference to glass tanks and to annealing furnaces, have been outlined by R. Günther.[60] J. P. Poole[61] has presented the design of a large-scale experimental pot furnace with a rotating hearth, and has discussed firing procedures and techniques used to determine melting and fining times that are comparable with those obtained in continuous tank furnaces. H. S. Y. Gill[62] has presented a general paper on glass tank furnaces.

The importance of obtaining the best life from refractories has also led to a number of papers. The economics of cooling glass tanks by forced air has been discussed by C. E. Gould[63] who concludes that, although cooling of tank wall blocks gives increased life, financial advantage follows only when increase in life exceeds a certain value. General profit and loss formulae have been worked out which can be applied in any particular case.

A. C. Lea[64] has discussed the rate of oxidation of granular and bonded silicon carbide in various atmospheres. C. E. Gould[65] has described a method of deducing the contour of tank blocks after use in the furnace and has shown that variability of glass level in the tank must be taken into account as well as temperature and temperature gradient. Applications were given in connexion with the assessment of the effects of the variation in the glass level, the iron oxide content of the glass and the temperature and in comparing different refractories. W. M. Hampton[66] also has presented proof that the shape of the erosion of side-wall blocks is predictable from the vertical temperature gradient in the glass and the variation in the solubility of the refractory with temperature as determined in a laboratory test, and that an accurate control of the glass level tends to accentuate the wear at the flux line and to reduce the life of the block. R. G. Abbey[67] has claimed that low production rates permit the use of basic (magnesite) checker brick in standard settings with alumina–silica superstructures, and that severe service requires basic regenerator crowns and uptakes in conjunction with basket weave settings which should be at least 18 courses deep. Refractories for glass furnaces have been discussed generally by W. F. Rochow.[68]

With a view to finding the most suitable refractories to use to avoid cord formation in tanks, R. Schmidt and M. Thomas[69] devised a test in which the glass was melted in a platinum crucible together with a cube of the refractory, and was then drawn out finely and cut to form threads. These were examined by passing them through the fingers, and the number of cordy threads was expressed as a percentage of the glass melt. Highly acid bricks made from natural sand, and magnesite bricks, were found satisfactory but caused trouble through instability of volume; natural quartzite was good in all respects but could not be obtained in sufficiently large blocks. It was also found that the corrosive bivalent oxides of lead and barium had a mutually retarding action, so that glasses containing both oxides could be produced satisfactorily in the normal refractories.

The attack of glass melts on platinum in reducing atmospheres has been discussed by J. Fischer.[70]

Methods of obtaining improved and more efficient melting by the use

of gas of higher calorific value than ordinary producer gas have also received attention, notably in a paper by M. Fanderlik,[71] in which he discusses the use of grid gas made by the Lurgi process in Czechoslovakia. Good results have been obtained when melting optical glass and special pot-melted glasses for the manufacture of artificial jewels. With 20% excess air in a furnace at 1300° c. the furnace efficiency was 34% against 25% with common producer gas. Grid gas has high calorific value and is of high purity; it may be used for heating glory holes, edge-burning, and lampworking generally.

Prospects for the use of oxygen in the glass industry were referred to by D. J. O. Brandt,[72] who concluded that no promising case could be made out for this. Oxygen could, however, be used for the production of a good-grade gas from poor-grade solid fuel, as is done in the Lurgi process.

The application and potentialities of town gas in the handblown domestic glass industry has been discussed by J. A. Tomes.[73] Some developments in gas producers have been discussed anonymously,[74] and *Fuel Efficiency News*[75] has published some notes on gas producer practice. Other papers relating to fuels include one by R. Pigrais and W. R. Bulcraig[76] on the use of fuel oil in glass furnaces, which has been published in summary, and a discussion of the efficiency of various types of recuperators used with tank furnaces, by R. Günther.[77]

Analysis and testing of glass

There is little new to report on methods of chemical analysis specifically applied to glass.

B. B. Osthaus[78] has discussed the use of quinaldic acid as a reagent for the determination of zinc in silicate analysis, which he claims is more selective than 8-hydroxyquinoline or 8-hydroxyquinaldine. G. Satlow[79] has discussed the quantitative analysis of mixed spun yarn made from asbestos, glass, and organic fibres. The analysis of silicates by rapid methods has been described by W. Daubner,[80] and the volumetric determination of silica has been discussed by H. N. Wilson.[81]

P. J. Ehring and P. C. Chao[82] have described a method for the determination of alkali metals in silicates, which is claimed to be much simpler in manipulative details than the Lawrence Smith method. This involves dissolving the sample with sulphuric and hydrofluoric acids and igniting to remove silicon and other elements. The residue is ignited at a higher temperature to convert most of the aluminium and iron sulphates to oxides. Ammonium hydroxide is added to the water suspension of the residue, yielding a readily filtered oxide and hydroxide mixture. Calcium and magnesium are efficiently precipitated as the oxalate in 85% acetic acid solution by the hydrolysis of ethyl oxalate. The alkali metals are then recovered as the sulphates from the resulting filtrate.

Literature on the use of physical methods in the chemical analysis of glasses has been reviewed by J. Fischer,[83] with special reference to potentiometry, conductimetry, photometry, polarography, and flame spectrophotometry. It is apparent that much further work will be needed before these methods can replace the ordinary chemical methods of analysing glasses.

In recent years, physical properties have been used increasingly by glass technologists as routine tests for control of production. A. T. Coe[84] has discussed the use of density measurements in assessing the quality of container glass, and has described an apparatus which allows six separate determinations of density to be carried out simultaneously. The method depends on measurement of the temperature differences required to 'float' the pieces of glass in binary liquids, the temperature differences being translated into density differences by means of the known temperature coefficient of density of the liquids.

Routine control by density measurements of glass during manufacture was also discussed by P. Staton and P. Maycock,[85] who pointed out that, when the glass composition fluctuations are within reasonable limits, a parallelism exists between density and thermal expansion coefficient value. In cases where close control of thermal expansion may be essential it is thus possible for the primary control to be carried out by density determinations, which are rapid and inexpensive, the thermal expansion measurements desirable for purposes of confirmation being made at less frequent intervals. Control of production by measurement of refractive index is suggested by R. E. Bastick and C. E. Gould,[86] who have studied refractive index and density measurements as alternatives for day-to-day control of glass composition during manufacture. They conclude that the refractive index is the more suitable, since it is easier to measure than density and the effects of composition change on refractive index are more marked. Refractive index measurements for assessing variability in glass quality and as a control of the efficiency of batch mixing in the manufacture of lead glass tubing are also reported on favourably by M. Manners and J. H. Partridge.[87]

A new optical thickness gauge for flat glass has been described by L. I. Shusset.[88]

A test of the degree of annealing by comparing the refractive index of the sample against a standard has been patented by the American Optical Co.[89]

Durability

The continuously increasing use of glass containers for the storage of sensitive chemicals, drugs, colloidal solutions, blood, and various sera over long periods, and for purposes necessitating the sterilization of the container each time it is used, has contributed to maintaining or even increasing the importance of devising glasses of improved durability, or methods of obtaining temporary improvements in durability, and also of devising tests for the determination of the durability of containers to be used for specific purposes.

A report of a collaborative study on the chemical durability of borosilicate glass, surface-treated lime glass, and untreated lime bottle glass has been published by the U.S. National Formulary Committee,[90] together with reports on tests of the effect of shape and size of ampoules, etc., and on the autoclave testing of containers for drugs with acid test-liquid.

P. Bremond[91] has discussed the solvent action of water and aqueous

solutions on the surface of glass, with particular reference to disintegration in the form of flakes.

In a study of the effect of rinsing bottles with various solutions with a view to improving chemical durability, K. C. Lyon[92] found that a copper chloride solution was the most effective in reducing the subsequent rate of extraction of alkali. R. D. Smith and P. E. Corbin[93] made a comparison between the attack by NaOH and that by sodium silicate solutions on various glasses, and found that, below approximately 0·5N. Na_2O the rate of attack by NaOH is the greater, but at higher normalities the rate of attack by silicate solutions may be more than twice that of the equivalent NaOH solutions.

The hygroscopicity of soda-lime container glasses has been studied by F. R. Matson,[94] who kept powdered samples of commercial bottles and laboratory melts in an atmosphere of 98% relative humidity at 100° F. for three days.

H. Jebsen-Marwedel and K. Dinger[95] have studied the comparative effect of different types of pre-treatment on the leachability of fresh glass surfaces, and found that treatment with $SO_2 + O_2$ gave a high reduction in the amount of alkali which could be removed, as compared with untreated glass.

The forces between a liquid and a solid were studied by E. C. Marboe and W. A. Weyl[96] by observation of the degree of release of gas bubbles from a supersaturated solution of CO_2 in a container of the solid (e.g. glass). No bubbles were released if the clean glass surface contained no heavy metal ions. If the glass contained Cu^{2+} or Pb^{2+} in its structure, or if the surface had been treated with a Pb or Cu salt, marked evolution of gas occurred. Similar treatments of degassed colloidal $Si(OH)_4$ or $Al(OH)_3$ or of weathered glass surfaces did not produce gas bubbles, and it was suggested that a certain 'rigidity' of the surface is necessary for evolution of gas.

The reactions of ions in aqueous solution with glass and metal surfaces have been discussed by J. W. Hensley.[97]

M. K. Roman, E. C. Marboe, and W. A. Weyl[98] have found that the hygroscopicity of a soda-lime-silica glass was increased by treatment of the powder with HCl and decreased by treatment with $CaCl_2$, $SnCl_2$, and $MgCl_2$ (slightly) and very markedly with $BaCl_2$. This effect follows the order of the ionic potentials. The ions Pb^{2+} and Zn^{2+} caused very marked decrease of hygroscopicity owing to their polarizability. It is pointed out that these effects may have applications in protecting glass-fibre products from moisture.

Physical properties

It is clearly unnecessary to emphasize the fact that any theory concerning glass structure must be capable of explaining the physical properties of glasses, and that the physical properties constitute the final test of the validity of any such theory. For this reason, therefore, any theoretical treatment in which an endeavour is made to correlate physical properties with structural considerations must be regarded as of outstanding interest. One particularly noteworthy contribution in this field has been the publication of J. M. Stevels' 'Progress in the theory of

the properties of glass'[99] as the second of the Monographs published in Holland on the progress of research in that country. Other papers of a general type have been published by R. Vieweg,[100] who has compared the physical properties of organic and inorganic glasses, and by J. R. van Wazer, [101] who discusses the physical properties of solutions of a sodium phosphate glass. Other papers dealing with specific properties in relation to structure are referred to in the various sections which follow.

Thermal expansion and other thermal effects.—Effects which annealing produces on the expansion characteristics of borosilicate thermometer glasses, including the changes produced by raising the equilibrium temperature, have been studied by A. Q. Tool and J. B. Saunders.[102]

G. O. Jones[103] has discussed reversible thermal after-effects in glass which are responsible for zero depression in mercury-in-glass thermometers. In his mathematical treatment, he shows that thermal after-effects of the right order of magnitude can be explained by postulating a distribution of local composition corresponding to differences of only a few per cent. in the relative proportions of the main constituents. The effects are assumed to be delayed elastic strains, resulting from stresses which originate between these regions of different composition due to differing contractions during cooling from the annealing temperature. The author points out that as large coefficients of expansion and large delayed elastic effects are usually found together in glasses containing a high proportion of soda, potash, or both, the effect will usually be in the direction noted, but the theory does not exclude effects in the reverse direction.

A. Danzin[104] has compared experimental values of the expansion coefficients of six glasses with calculated values based on the formula $\alpha = \Sigma pi.ai$ where pi is the weight content of the constituent oxide i, and ai is a coefficient characteristic of the same oxide. The calculated values were too high by 1 or 2% except for one barium glass where it was low by 4%.

Strength and other mechanical properties.—The literature on the strength of glass has been enhanced by the publication during the year of R. N. Haward's 'The strength of plastics and glass'[105]; this covers too wide a field for even a summary review here.

A critical review of previous work on the strength of glass (based on the Griffith flow theory and on later theories of the strength of solids) has been published by G. O. Jones.[106] The author believes that the Griffith theory has still important application to the case of glass, particularly at ordinary temperatures, and that is, in fact, the only basis for a consistent explanation of the phenomena.

C. Gurney with S. Pearson[107] has extended his study of delayed fracture of glass to a consideration of the effect of surrounding atmospheres. Experiments were made in air and *in vacuo*; the effect of heating *in vacuo* to drive off absorbed atmospheric constituents was also tried. Curves plotting stress against mean time to fracture, of a number of specimens, show that the tendency to break after long periods of light or medium loading decreases with decrease of pressure; at 10^{-5} mm. Hg after heat treatment, the curves were very flat showing that the main cause of delayed fracture is attack of the glass by atmospheric constituents. It was found that the harmful constituents could be supplied by capillary

liquid contained in surface cracks and by migration from surface layer as well as by direct attack from the gaseous phase.

E. Poncelet[108] has continued his study of glass fracture by reviewing, in a well illustrated paper, the phenomenon of fracture caused by tension in vitreous bodies.

Tests have been made by N. J. Thompson and E. W. Cousins[109] to determine whether or not glass windows would be of value in preventing building damage from internal explosions involving combustible dusts or vapours. It was found that the effective strength of glass panes increases in an approximate linear ratio with increased rate of pressure application, and it was concluded that window glass is of dubious value for explosion venting purposes, except possibly for explosions of high pressure but of very short duration.

A. Hoffman and L. von Reis[110] have described load tests with cracked reinforced (wired) glass designed to ascertain what residual bearing strength was possessed by reinforced glass after the panes were cracked and the pieces held together only by the wire insert.

Holophane Ltd.[111] have patented a process of rendering glass shock-resistant by treating it with HF after heat treatment, to remove the surface layer which is likely to contain minute flaws.

An unusual test for the strength of airplane windscreens has been described by P. Kangas and G. L. Pigman[112] who, noting that, on the average, collisions between birds and aircraft are reported more frequently than once a day, and that in about 25% of the cases the bird is struck by the windscreen, devised a special air-gun which shoots chicken and turkey carcases at windscreens at speeds of up to 450 m.p.h. Laminated glass with a thick polyvinyl butyral plastic interlayer, which extended beyond the glass edges on all sides, for bolting to the frame of the aircraft, was found far superior to other types of screens tested. Tests of glasses for aircraft windscreens have also been discussed by K. Egner.[113]

P. A. Koch and G. Satlow have extended their study of glass fibres to a consideration of the fundamentals of dry-strength and of dry-stretching tests,[114] the relation between fineness and strength,[115] and the quantitative analysis of yarn made from asbestos, glass fibres, and organic fibres.[116] They have also published illustrated tables summarizing details of the development, manufacture, and properties of glass fibres.[117]

H. Rawson[118] has discussed the theory of stresses in two-component glass-to-metal tube seals. The practical aspects of the resistance of bottles to bursting have been discussed by R. E. Mould and J. M. McCormick,[119] and the testing of bottles for durability has been described by K. H. Borchard and M. Schulze.[120] The creep of glass at high temperatures has been discussed by C. Crussard.[121] K. Georg[122] has discussed the hardness of optical glasses, and E. W. Taylor[123] has published a table of the hardness of some well-known types of optical glass.

Surface properties.—R. Ramsauer[124] has discussed the boundary-layer friction on glass as a problem of adsorption. This is the type of friction which occurs when the two surfaces are so close together that shearing must take place, not in the free-flowing molecules of the liquid lubricant, but in the oriented layers adsorbed on the surface of the solid.

E. May[125] has discussed the influence of surface strain in optical glasses.

Wetting of glass surfaces has been briefly discussed by G. Haase,[126] and the use of organic silicon compounds to render glass surfaces water-repellent has been patented by British Thomson-Houston Co. Ltd.[127] and Corning Glass Works.[128]

Electrical properties.—Processes occurring in glass subjected to a constant electric field between two electrodes, which involve migration of ions and physical modification of the glass–metal contact surfaces, have been discussed by J. Peyssou.[129]

A. Danzin[130] has derived a formula for expressing the electrical resistance of silicate glasses which is not valid, however, except for glasses containing only basic elements with 35–70% SiO_2 (i.e. containing no acidic constituents such as B_2O_3, P_2O_5 etc. in addition to SiO_2).

In a previous paper, reported last year, A. E. Dale and J. E. Stanworth outlined the development of 'solder' glasses and some of their electrical applications. They have now given[131] detailed results of investigations into the borate systems of lead, barium, and zinc which previously had been found the most likely to yield glasses of the desired properties.

A. Danzin and P. Meunier[132] have measured permittivity (ϵ) and loss angle (δ) in the range 300 kilocycles to 100 megacycles for glasses of composition SiO_2, 40–75% and $R_2O + RO$, 10–40% in an electric field of 400–1500 v./cm. and have shown the results diagramatically.

Measurements by G. F. Rynders O. H. Grauer and D. Hubbard[133] of the durability and hygroscopicity of a series of glasses containing 51–91% SiO_2 and their behaviour as electrodes in solution indicated that the glass SiO_2, 86 and Na_2O, 14% would function well as a hydrogen electrode, but satisfactory electrodes could not be made from this glass because it has a high liquidus temperature and tends to devitrify. The glasses could be divided into three groups according to their durability at p_H 4·6, viz: (1) readily soluble (SiO_2 content less than 81%), (2) showing differential solution of the constituents leaving a swollen silica-rich layer (81–89·5% SiO_2), and (3) relatively only slightly soluble (SiO_2 content greater than 91%). Only in the region of swelling were good electrodes obtained. The departure from the linear voltage-characteristics of electrodes made from glasses of high hygroscopicity and poor durability were similar to that of a punctured electrode and approached the value of a calomel half-cell. The non-linear characteristic was not due to a response to sodium.

G. A. Perley[134] has reviewed the literature on the composition of p_H responsive glasses and has summarized data obtained from his own study of over 500 different compositions. He has also discussed the function of the alkali metals and of the alkaline-earth metals in these glasses.

Optical properties.—The spectral-transmissive characteristics of some German glasses together with compositions have been given by R. Stair and co-workers.[135] R. Stair has also described[136] a photoelectric meter for the shade-number classification of industrial eye-protective glasses.

F. A. Molby[137] reported studies on the refractive index and coefficients of expansion of optical glasses at low temperatures, by observation of

the changes of optical thickness with temperature, using a Pulfrich interferometer.

Kuan-Han Sun[138] has given compositions, Abbe values (reciprocal dispersions) and melting points for some experimental aluminate glasses, and along with J. J. Rothermel and A. Silverman[139] has studied glasses of the $PbO-WO_3-P_2O_5$ system, which are useful for optical purposes on account of their high refractive indices and relatively low dispersions.

A series of patents have appeared during the year in the name of the Eastman Kodak Co. and H. K. Sun[140] covering various compositions for optical glasses.

E. M. Levin and H. F. McMudie[141] have constructed a phase-equilibrium diagram of the system $BaO-B_2O_3$ constructed from data obtained essentially by the quenching method, and have presented a curve showing indices of refraction of the quenched glasses.

The optics of curved glass has been discussed by D. W. Dunipace.[142]

The properties of surface films which may be produced on glass surfaces when treated in various ways, and the structure of films applied to glass surfaces, have been dealt with in a number of papers. Some of these are directed towards the reduction of reflection from the surfaces of the glass components of optical instruments, but in one or two cases the changes in reflectivity are used as a measure of surface deterioration.

Reduction of optical reflectivity of glass surfaces resulting from ion bombardment has been reported by J. Koch, [143] and the structure of calcium fluoride films evaporated on polished glass surfaces has been studied by J. Bannon and C. E. Curnow.[144] Methods of imparting anti-reflection qualities to glass have been the subject of a U.S. Department of Commerce Report[145] and have also been discussed by F. H. Nicoll.[146] A. Vasicek[147] has studied the reflecting power of glass with a thin and with a thick film.

Coating of microscope eyepiece lenses has been discussed by G. R. Lane.[148] F. Suhner[149] has measured the thickness and indices of coatings on glass by polarimetric methods. B. Long[150] has studied the tarnishing of polished glass surfaces including those of the resistant borosilicate crowns, and has found that this is due to the action of humid air modified by CO_2 and greasy materials. The dimming test as proposed and amended by F. L. Jones[151] and also by E. R. Rachel with C. A. Glaser[152] was recommended for predicting the behaviour of optical surfaces under normal conditions of use.

A method for the simultaneous determination of the refractive index, reflection, and thickness of a thin layer on a glass surface in polarized light has been described by F. Abeles.[153] K. Hamner[154] has described improvements of glass reflection by metal oxide layers. N. Cabrera and J. Terrier[155] have studied the structure and the optical properties of thin metallic coatings. M. Hack[156] has discussed the tolerance for scratches and for cords in spectacle lenses. The manufacture of boric acid glass for luminescence studies has been described by M. Kasha,[157] and the optical and electrical properties of zinc silicate phosphors have been discussed by E. Nagy[158]

Viscosity.—Jas. P. Poole[159] studied Na_2O, K_2O and NaK silicate glasses containing 10–40 mol. % alkali in relation to viscosity at low temperatures.

J. P. Poole, with M. Gensamer,[160] has also reported a systematic study of the effect on viscosity at annealing temperatures of substituting the oxides Na_2O, K_2O, CaO, MgO, SrO, BaO and Al_2O_3 for SiO_2 and for each other in simple 3- and 4- component glasses, the ranges in composition covering most commercial silicate glasses; the results are given in 38 curves. The same worker has also described[161] the fibre elongation method used for the above-mentioned determinations.

Crown and flint glasses have been tested by E. W. Taylor[162] for plastic deformation using a hardness microtester, and W. C. Levengood and H. R. Swift[163] have discussed the lateral growth of cutter marks in glass.

Coloured glasses

S. D. Stookey[164] conducted experiments which indicated that gold dissolves in glass in an oxidized state, not as metallic Au. The glass is practically colourless as long as the Au remains oxidized, but with reducing conditions free Au is formed and the characteristic colour appears. Ions of Sn, or other multivalent ions, act as reducing agents at relatively low temperatures. Similar results were obtained with Ag and Cu glasses. In the absence of a reducing agent, glasses can be cooled to room temperature and reheated and still retain the metal in an ionic state, the glass remaining colourless.

The changes in the transmission in the range 250–1000 $m\mu$., due to the addition of up to 2·7% of CeO_2 to a soda–lime–silica glass and to a lead flint glass, and up to 4·77% of CeO_2 to a borosilicate glass, have been measured by J. A. Kapnicky and W. A. Koehler.[165]

T. Forland and W. A. Weyl[166] have shown that the striking of a cadmium sulphide glass is similar to the separation of sulphide ores from an original magma, and have explained the two phenomena by derivation from experiments with model substances, i.e. halogen ions which are of a less corrosive nature than silicate and sulphide ions, and by interpretation of the experiments on the basis of Fajan's theory of the deformation of ions. The colour and magnetic properties of some Co compounds have been discussed by J. E. Stanworth[167] with reference to the electron rings. The spectral transmissions and colours of new neutral glasses developed by Chance Bros. for use in colorimetry have been given by W. D. Chesterman[168] who has also compared these glasses with older types obtainable in this country and in Germany.

A. Dietzel and R. Boncke[169] have refuted the suggestion of Beyersdorfer[170] that the yellow or brown coloration in glasses containing titanium is caused by lower oxides of titanium since, it is stated, these produce a cobalt blue colour; they reaffirm the view that the brown coloration is caused by the simultaneous presence of iron with the titania, because TiO_2 alone has no colouring action.

A. Dietzel[171] has discussed the formation of cuprous sulphide in copper glasses. R. J. Callow[172] has studied the effects of increasing quantities of fluorine on some easily measured properties of the soda–lime–silica system on the development of opalescence and on the amount of fluorine lost in melting. P. Beyersdorfer[173] has discussed the opacification of glasses with fluorides.

New manufacturing methods and uses of glass

P. Balderman[174] has described a special method of glass melting which involves the production of an intermediate (semi-melted) product for use in the batch.

K. Riess and co-workers[175] have discussed the new photosensitive glass in which a permanent photographic image of exceptional fidelity can be reproduced after exposure to ultra-violet light and development by heat. This development has been discussed also by S. D. Stookey[176] who is co-patentee with Corning Glass Works for this process (B.P. 570,111 and B.P. 597,089).

Glass containing mica and glass containing prefired ceramic material, for use as dielectric heating materials, have been patented respectively by Standard Telephone and Cables Ltd.[177] and G. Morton.[178] The manufacture and properties of glass insulators for electric power lines has been discussed by M. Kanzler.[179]

E. M. Guyer[180] has discussed the electric welding of glass, and concludes that up to 600° C. high-frequency heating is effective ; at higher temperatures, heating by normal electrical conduction is preferable ; at 1200° C. and over, soda-lime and certain other glasses can be melted and worked by induction heating.

A. Wendler[181] has described the new Swiss A.W. 150 single-mould machine which uses the suck-and-blow method, and E. W. Hunter and L. E. Norton[182] have described the principles underlying the making of glass containers by automatic gravity-fed machines. The fully automatic production of stemware both in this country[183] and in the United States[184] has been reported. A new liquid honing process for cleaning glass moulds has been described by British Vapour Blast Ltd.[185] The Libbey-Owens-Ford Glass Co.[186] have patented a means for separating glass sheets in storage by means of a layer of dry, powdered, non-abrasive material which is attached by means of an electrostatic charge. The commercial production of optical components by grinding with diamond tools and wheels has been described by K. Georg.[187] It may be mentioned that this technique has been in use by certain firms in Great Britain for considerably over 15 years.

D. M. Considine[188] has patented a glass-lined target tube for radiation pyrometers and C. T. Gould[189] has patented a glass-lined mould for shaping plastic material. Corning Glass Works[190] have published information on an electrically conductive coating for glass which makes possible an electrical glass coffee maker which requires no stove or hot plate. J. K. Davis[191] has patented a method of preventing the blackening of glass by mercury vapour, by treating the glass with water at a temperature of 20–80° C. until the glass has attained maximum chemical stability, and then heating the glass for about five minutes at 750° C.

New developments in the manufacture of thermometers have been discussed by B. Siede[192] ; the use of glass in the chemical industry has been surveyed by J. H. Koenig[193] and by J. W. O. Pie and W. J. Ward[194] and also J. G. Window.[195] Laminated window glass with a transparent conducting interlayer which can be heated electrically has been patented by Pittsburgh Plate Glass Co.[196]

Miscellaneous

The Society of Glass Technology has reported on standardized dimensions of glass-to-metal seals of the sandwich and bead types and a standard method for determining stresses therein.[197] The electric lamp and radio valve industry owes a debt of gratitude to J. H. Partridge[198] for his excellent monograph on glass-to-metal seals published during the year by the Society of Glass Technology. A kinetic test for evaluating the adhesion of molten glass to metal, expressed in terms of the highest metal temperature at which a drop of molten glass shows no adhesion, has been described by J. A. Kapnicky and co-workers.[199]

J. M. Florence and co-workers[200] have studied the transmittance of near-infra-red energy by binary glasses, and have given values for lead silicate glasses of higher lead content than have previously been reported in the literature. J. V. Fitzgerald[201] has reported on experiments in which glass specimens were irradiated with deuterons which changed some of the ^{23}Na in the glass to the radioactive isotope ^{24}Na. When heated in contact with a de-alkalizing agent (clay or Cr_2O_3), some of the radioactive Na was transferred from the glass to the agent. After cooling, the agent was scraped from the glass surface and radio-assayed; the activity was found to increase with time and temperature. From the composition and distribution of induced radioactive Na, the effectiveness of the dealkalizing agent was determined.

The use of control instruments in the glass industry has been discussed by J. R. Green[202] and H. J. Velten.[203]

The various organic materials available for cementing glass to glass have been discussed by F. Moser and L. M. Humphrey,[204] who also describe methods of testing strength of bonding and the effects of the curing cycle upon the strength and the clarity of the bond obtained from synthetic resin adhesives.

H. Moore[205] has presented a review of post-war investigations into the domestic glassware industry of Germany based on data disclosed in BIOS and FIAT reports. Post-war structural changes in the German glass industry have been discussed anonymously,[206] also the glass industry in Italy.[207] Statistics concerning Russian glass, including production figures for 1947 and rate of drawing Fourcault glass, have also been published.[208] It is stated that a drawing rate in excess of 80 metres/hr. was planned for 1948. W. E. S. Turner[209] has given his impressions of glass technology in Czechoslovakia after a visit to that country.

J. A. Hedvall[210] has briefly outlined the founding of the Institute for Silicate Research at Göteborg, Sweden, and its general scope, and has given some notes on work carried out there in recent years. A new technical organization to be known as the Swedish Society of Glass Technology was formed during the year.[211] The Institut National des Silicates, Brussels, has also been described.[212] H. Moore[213] has described the role of the Department of Glass Technology, Sheffield University. M. Branchereau[214] has discussed the role of glass works control laboratories. The application of statistical methods to the glass industry has been discussed by F. W. Preston[215] and the statistical treatment of density measurements has been reported by K. Daeves.[216]

References

[1] Cox, S. M., *J. Soc. Glass Tech.*, 1948, **32** (149), 340
[2] Weyl, W. A., ibid. (148), 247
[3] Jones, G. O., ibid. (149), 382
[4] Idem., ibid., 1949, **33** (150), 64
[5] Douglas, R. W., ibid. (152), 138
[6] Andreasen, A. H. M., ibid., 163
[7] Douglas, R. W. and Jones, G. O., ibid., 1948, **32** (149), 309
[8] Stanworth, J. E., ibid., 366
[9] Smekal, A. G., ibid., 378
[10] Sheybany, H. A., *Verres et Refract.*, 1948, **2**, 127, 229, 363 ; 1949, **3**, 27
[11] Weyl, W. A., *J. Amer. ceram. Soc.*, 1949, **32** (11), 367
[12] Fricke, R., *Glastech. Ber.*, 1949, **22** (17), 385
[13] O'Daniel, H., ibid., 1948, **22**, 11
[14] Ruess, G., ibid., 1949, **22**, 173
[15] Smekal, A., ibid., 177
[16] Blau, H. H. and Johnson, J. R., *Ohio St. Univ. Eng. exp. Sta. News*, 1948, **20** (5), 45
[17] Jones, F. L. and Kreidl, N. J., *J. Soc. Glass Tech.*, 1949, **33** (153), 239
[18] Weyl, W. A., ibid., 220
[19] Gillod, J., *Verres et Refract.*, 1949, **3**, (3), 161
[20] Hummel, F. A., *J. Amer. ceram. Soc.*, 1949, **32** (10), 320
[21] Poole, J. P., ibid. (7), 237
[22] Sawyer, E. C., *Ohio St. Univ. Eng. exp. Sta. News.*, 1948, **19** (2), 57
[23] Glowka, R. and Strange, O., *Glashütte*, 1949, **75** (9), 168
[24] Plumat, M., *Silicates Industr.*, 1949, **14** (6), 125
[25] Jebsen-Marwedel, H., *Glastech. Ber.*, 1949, **22**, 169
[26] Dietzel, A., ibid., 246
[27] Quaiser, N., *Glashütte*, 1949, **75** (8), 157
[28] Stuckert, L. and Rauter, F.-J., *Glastech. Ber.*, 1948, **22**, 108
[29] Schmidt, A. W., ibid. (5/6), 108
[30] Johnston, S. J., *Industr. Chem. chem. Mfr.*, 1949, **25** (291), 247
[31] Anon., *Ceramic Ind.*, 1948, **51** (3), 82
[32] Menzel, H. and Adam, J., *Glastech. Ber.*, 1949, **22** (12), 237
[33] Kröger, C., ibid., 248
[34] Sun, K. H., *Glass Ind.*, 1949, **30**, (4), 199
[35] Jebsen-Marwedel, H., *Glastech. Ber.*, 1948, **22**, 4
[36] Idem., *Silicates Industr.*, 1949, **14**, 21
[37] Idem., ibid., 47
[38] Rodnikova, V. V., *Steklo i Keram.*, 1949, **6** (3), 10
[39] Paschkis, V., *Bull. Amer. ceram. Soc.*, 1948, **27**, (11), 450
[40] Bonnier, E., *Verres et Refract.*, 1948, **2** (5), 288
[41] Anon., *Glass Ind.*, 1949, **30** (10), 556
[42] Dunn, K., ibid. (7), 391
[43] Blackman, M., *Proc. roy. Soc.*, 1948 [A], **194** (1037), 147
[44] Lindroth, S., *J. Amer. ceram. Soc.*, 1949, **32**, 198
[45] Lepingle, M., *Silicates Industr.*, 1949, **14** (5), 109
[46] Bateson, H. M., *J. Soc. Glass Tech.*, 1949, **33** (150), 27N
[47] Kröger, C., *Glastech. Ber.*, 1948, **22** (5/6), 86
[48] Plumat, M., *Silicates Industr.*, 1949, **14**, 125
[49] Faick, C. A., *J. Res. nat. Bur. Stand.*, 1949, **42**, 153
[50] Quadrelli, M., *L'Industr. della Ceram. Sil.*, 1949, **2** (4), 15
[51] Enright, D. P., *J. Amer. Ceram. Soc.*, 1949, **32** (11), 351
[52] Dietzel, A., *Glashütte*, 1948, **75** (7), 125 ; 1949, **75** (8), 159
[53] Beyersdorfer, P. and Jockmann, F., ibid., 1948, **75** (1), 5
[54] Newkirk, T. F. and Tooley, F. V., *J. Amer. ceram. Soc.*, 1949, **32** (9), 272
[55] Peyches, I., *J. Soc. Glass Tech.*, 1948, **32** (149), 399
[56] Meigh, E., *Times Rev. Indus.*, 1948, **2** (23), 18
[57] Anon., *Glashütte*, 1949, **75** (12), 237
[58] Howard, G. E., *Glass Ind.*, 1948, **29**, 615, 656
[59] Soc. Glass Tech., *J. Soc. Glass Tech.*, 1949, **33** (150), 19
[60] Gunther, R., *Glastech. Ber.*, 1948, **22**, 50

[61] Poole, J. P., *J. Amer. ceram. Soc.*, 1949, **32** (7), 233
[62] Gill, H. S. Y., *J. Soc. Glass Tech.*, 1949, **33** (152), 95N
[63] Gould, C. E., ibid. (151), 82
[64] Lea, A. C., ibid. (150), 27
[65] Gould, C. E., ibid., 5
[66] Hampton, W. M., ibid., 1948, **32** (147), 173
[67] Abbey, R. G., *Glass Ind.*, 1949, **30**, 268
[68] Rochow, W. F., ibid., 205
[69] Schmidt, R. and Thomas, M., *Glastech. Ber.*, 1948, **22**, 17
[70] Fischer, J., ibid., 1949, **22** (12), 262
[71] Fanderlik, M., *J. Soc. Glass Tech.*, 1949, **33** (151), 89
[72] Brandt, D. J. O., ibid., 103
[73] Tomes, J. A., *Glass*, 1948, **25** (12), 355
[74] *Coke and Gas*, 1949, **11** (123), 273
[75] *Fuel Effic. News*, Aug. 1949
[76] Pigrais, R. and Bulcraig, W. R., ibid., Nov. 1948 ; *Nature*, 1948, **162**, 952
[77] Gunther, R., *Glastech. Ber.*, 1949, **22** (15), 321
[78] Osthaus, B. B., *J. Amer. ceram. Soc.*, 1949, **32** (8), 256
[79] Satlow, G., *Glastech. Ber.*, 1949, **22**, 121
[80] Daubner, W., *Mitt. Deut. keram. Ges.*, 1949 (1), 56
[81] Wilson, H. N., *Analyst*, 1949, **74** (877), 243
[82] Ehring, P. J. and Chao, P. C., *Analyt. Chem.*, 1949, **21** (4), 507
[83] Fischer, J., *Glastech. Ber.*, 1949, **22** (17), 390
[84] Coe, A. T., *J. Soc. Glass Tech.*, 1949, **33** (153), 199
[85] Staton, P. and Maycock, P., ibid. (152), 188
[86] Bastick, R. E. and Gould, C. E., ibid. (150), 51
[87] Partridge, J. H., ibid., 59
[88] Shusset, L. I., *Bull. Amer. ceram. Soc.*, 1949, **28** (10), 377
[89] American Optical Co., B.P. 584,885
[90] U.S. National Formulary Committee, *Bull. Nat. Formulary Comm.*, 1949, **17**, **41**, 61, 48
[91] Bremond, P., *Verres et Refract.*, 1948, **2**, 15
[92] Lyon, K. C., *J. Amer. ceram. Soc.*, 1949, **32** (2), 46
[93] Smith, R. D. and Corbin, P. E., ibid. (6), 195
[94] Matson, F. R., ibid., 121
[95] Jebsen-Marwedel, H. and Dinger, K., *Glastech. Ber.*, 1948, **22**, 57
[96] Marboe, E. C. and Weyl, W. A., *J. Soc. Glass Tech.*, 1948, **32**, 281
[97] Hensley, J. W., *Ind. Eng. Chem.*, 1949, **41** (7), 1415
[98] Roman, M. K., Marboe, E. C. and Weyl, W. A., *J. Soc. Glass Tech.*, 1948, **32**, 260
[99] Stevels, J. M., 'Progress in the Theory of the Physical Properties of Glass,' (Amsterdam: Elseviers Pub. Co. Inc., 1948)
[100] Vieweg, R., *Glastech. Ber.*, 1949, **22** (16), 353
[101] Wazer, J. R. van., *Ind. Eng. Chem.*, 1949, **41** (1), 189
[102] Tool, A. Q. and Saunders, J. B., *J. Res. nat. Bur. Stand.*, 1949, **42**, 171
[103] Jones, G. O., *Proc. phys. Soc. Lond.*, 1948, **61** (346), 320
[104] Danzin, A., *C. R. Acad. Sci., Paris*, 1949, **228**, 561
[105] Haward, R. N., 'The Strength of Plastics and Glass' (London: Cleaver-Hume Press, 1949)
[106] Jones, G. O., *J. Soc. Glass Tech.*, 1949, **33** (151), 120
[107] Gurney, C. and Pearson, S., *Proc. phys. Soc. Lond.*, 1949, **62** (356 B), 469
[108] Poncelet, E., *Verres et Refract.*, 1949, **3** (3), 149
[109] Thompson, N. J. and Cousins, E. W., *J. Amer. ceram. Soc.*, 1949, **32** (10), 313
[110] Hoffman, A. and Reis, L. von., *Glastech. Ber.*, 1948, **22** (3/4), 64
[111] Holophane Ltd., B.P., 597,591
[112] Kangas, P. and Pigman, G. L., *S.A.E. Journal*, 1949, **57** (1), 54
[113] Egner, K., *Glastech. Ber.*, 1949, **22** (16), 358
[114] Koch, P. A. and Satlow, G., ibid., 1948, **22**, 103
[115] Idem, ibid., 1949, **22**, 161
[116] Idem, ibid., 121
[117] Idem, ibid., 226
[118] Rawson, H., *J. sci. Instrum.*, 1949, **26**, 25
[119] Mould, R. E. and McCormick, J. M., *Glass Ind.*, 1949, **30** (7), 381

[120] Borchard, K. H. and Schulze, M., *Glashütte*, 1949, **75** (10), 185
[121] Crussard, C., *Sheet Metal Industr.*, 1948, **25**, 2471
[122] Georg, K., *Glastech. Ber.*, 1949, **22** (11), 224
[123] Taylor, E. W., *J. sci. Instrum.*, 1949, **26** (9), 314
[124] Ramsauer, R., *Glastech. Ber.*, 1949, **22**, 205
[125] May, E., ibid. (13/14), 301
[126] Haase, G., ibid. (12), 262
[127] British Thomson-Houston Co. Ltd., B.P. 572, 740 ; B.P. 593,727
[128] Corning Glass Works, B.P. 588,762
[129] Peyssou, J., *Ann. Radioélect.*, 1948, **3**, 107
[130] Danzin, A., *C. R. Acad. Sci., Paris*, 1949, **228**, 487
[131] Dale, A. E. and Stanworth, J. E., *J. Soc. Glass Tech.*, 1949, **33** (152), 167
[132] Danzin, A. and Meunier, P., *C. R. Acad. Sci., Paris*, 1949, **228** (5), 391
[133] Rynders, G. F., Grauer, O. H. and Hubbard, D., *J. Amer. ceram. Soc.*, 1948, **31**, 269
[134] Perley, G. A., *Analyt. Chem.*, 1949, **21** (3), 391
[135] Stair, R., *Glass Ind.*, 1949, **30** (6), 331
[136] Idem, ibid. (8), 441
[137] Molby, F. A., *J. opt. Soc. Amer.*, 1949, **39** (7), 600
[138] Sun, K. H., *Glass Ind.*, 1949, **30**, 199, 232
[139] Rothermel, J. J. and Silverman, A., *J. Amer. ceram. Soc.*, 1949, **32**, 153
[140] Eastman Kodak Co. and Sun, K. H., U.S.P. 2,466,505–6–7–8–9–10 ; 2,472,447–8
[141] Levin, E. M. and McMurdie, *J. Amer. ceram. Soc.*, 1949, **32** (3), 99
[142] Dunnipace, D. W., *Glass Ind.*, 1949, **30** (10), 545
[143] Koch, J., *Nature*, 1949, **164**, 19
[144] Bannon, J. and Curnow, C. E., ibid., 1948, **161**, 136
[145] U.S. Dept. of Commerce O.T.S. Report P.B. 79,315
[146] Nicoll, F. H., *Glass Ind.*, 1948, **29** (9), 505
[147] Vasicek, A., *J. opt. Soc. Amer.*, 1949, **39** (5), 409
[148] Lane, G. R., *Nature*, 1949, **164**, 452
[149] Suhner, F., *Verres et Refract.*, 1949, **3** (1), 3
[150] Long, B., ibid. (2), 97
[151] Jones, F. L., *J. Amer. ceram. Soc.*, 1941, **24** (4), 119
[152] Rachel, E. R. and Glaser, C. A., Frankford Arsenal Ordnance Lab. Rpt. 27 (*Chem. Abstr.*, 1947, 177d)
[153] Abeles, F., *C. R. Acad. Sci., Paris*, 1949, **228** (7), 553
[154] Hamner, K., *Optik*, 1948, **3** (5/6), 495
[155] Cabrera, N. and Terrier, J., *Rev. d'Optique*, 1949, **28** (11), 635
[156] Hack, M., *Verres et Refract.*, 1949, **3**, 22
[157] Kasha, M., *J. opt. Soc. Amer.*, 1948, **38** (12), 1068
[158] Nagy, E., ibid., 1949, **39** (1), 42
[159] Poole, J. P., *J. Amer. ceram. Soc.*, 1949, **32**, 230
[160] Poole, J. P. and Gensamer, M., ibid., 220
[161] Poole, J. P., ibid., 215
[162] Taylor, E. W., *Nature*, 1949, **163**, 323
[163] Levengood, W. C. and Swift, H. R., *Glass Ind.*, 1949, **30** (6), 317
[164] Stookey, S. D., *J. Amer. ceram. Soc.*, 1949, **32**, 246
[165] Kapnicky, J. A. and Koehler, W. A., ibid., 1948, **31**, 321
[166] Forland, T. and Weyl, W. A., ibid., 1949, **32** (9), 267
[167] Stanworth, J. E., *J. Soc. Glass Tech.*, 1948, **32**, 224
[168] Chesterman, W. D., *J. sci. Instrum.*, 1949, **26** (5), 175
[169] Dietzel, A. and Boncke, R., *Glastech. Ber.*, 1949, **22**, 179
[170] Beyersdorfer, P., ibid., 1941, **19**, 349
[171] Dietzel, A., ibid., 1948, **22**, 63
[172] Callow, R. J., *J. Soc. Glass Tech.*, 1949, **33** (153), 255
[173] Beyersdorfer, P., *Glashütte*, 1949, **76** (1), 1 (2), 19
[174] Balderman, P., *Glass Ind.*, 1948, **29** (8), 447
[175] Riess, K., *Amer. J. Phys.*, 1948, **16**, 300
[176] Stookey, S. D., *Ind. Eng. Chem.*, 1949, **41** (4), 857
[177] Standard Telephones and Cables, Ltd., B.P. 586,521
[178] Morton, G., B.P. 590,183
[179] Kanzler, M., *Silicates Industr.*, 1949, **15** (8), 171
[180] Guyer, E. M., *Elect. Engng.* (*N.Y.*), 1948, **67**, 446

[181] Wendler, A., *Glashütte*, 1949, **75** (9), 167
[182] Hunter, E. W. and Norton, L. E., *J. Soc. Glass Tech.*, 1948, **32** (147), 44
[183] *Pott. Gaz.*, 1949, **74** (867), 989
[184] *Ceramic Ind.*, 1949, **53** (4), 70
[185] British Vapour Blast Ltd., *Glass*, 1949, **26** (8), 235
[186] Libbey-Owens-Ford Glass Co., U.S.P. 2,476,145
[187] Georg, K., *Glastech. Ber.*, 1949, **22** (13/14), 296
[188] Considine, D. M., U.S.P. 2,465,322
[189] Gould, C. T., B.P. 568,184
[190] Corning Glass Works, *Chem. Industr.*, 1949, **64** (3), 476
[191] Davis, J. K., U.S.P. 2,464,851
[192] Siede, B., *Glastech. Ber.*, 1949, **22** (17), 401
[193] Koenig, J. H., *Ind. Eng. Chem.*, 1949, **41** (10), 2107
[194] Pie, J. W. O. and Ward, W. J., *Chem. Industr.*, 1948, **63**, 782
[195] Window, J. G., *Chem. & Ind.*, 1948, 744
[196] Pittsburgh Plate Glass Co., U.S.P. 2,470,509
[197] Soc. Glass Tech., *J. Soc. Glass Tech.*, 1949, **33** (150), 77
[198] Partridge, J. H., 'Glass-to-Metal Seals,' (Sheffield : Soc. Glass Tech. 1949)
[199] Kapnicky, J., *J. Amer. ceram. Soc.*, 1949, **32** (10), 305
[200] Florence, J. M., ibid., 1948, **31** (12), 328
[201] Fitzgerald, J. V., *Glass Ind.*, 1949, **30**, 159
[202] Green, J. R., ibid., (3), 149
[203] Velten, H. J., *Ceramic. Ind.*, 1949, **53** (2), 67
[204] Moser, F. and Humphrey, L. M., *Glass Ind.*, 1949, **30** (3), 139
[205] Moore, H., *J. Soc. Glass Tech.*, 1948, **32** (147), 233
[206] Anon., *Glass Ind.*, 1949, **30** (7), 389
[207] Anon., ibid. (5), 275
[208] Anon., ibid., 1948, **29** (11), 650
[209] Turner, W. E. S., *J. Soc. Glass Tech.*, 1948, **32** (147), 60
[210] Hedvall, J. A. *Glastech. Ber.*, 1949, **22**, 201
[211] Swedish Society of Glass Technology, *Bull. Amer. ceram. Soc.*, 1949, **28** (6), 246
[212] Institut National des Silicates, Brussels, *Silicates Industr.*, 1949, **14** (7), 149
[213] Moore, H., *Research*, 1948, **1** (12), 562
[214] Branchereau, M., *Verres et Refract.*, 1949, **3** (4), 222
[215] Preston, F. W., *Bull. Amer. ceram. Soc.*, 1949, **28** (6), 225
[216] Daeves, K., *Glastech. Ber.*, 1949, **22** (11), 228

INTERMEDIATES AND COLOURING MATTERS

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ONCE again there has been very considerable publication on matters concerning intermediates and dyes. Nothing of outstanding novelty has appeared, however, and much of the patenting is along familiar lines covering improved manufacturing processes or, in dyestuffs, attempts to obtain improved properties by small changes in structure. Many of the dyestuffs patents, especially those on azo dyes for wool and cellulose acetate, disclose the use of new intermediates although they are not generally of fundamentally new types. The last few years have seen the introduction of colourless fluorescent compounds for improving the apparent whiteness of materials and it has been considered opportune to devote a separate small section to these compounds in this year's review.

There have been very few reports issued during the year on the German chemical industry, but various microfilms continue to become available dealing with works processes, research topics, conference minutes, etc. In addition, the FIAT Reviews of German Science for 1939–46 dealing with organic chemistry have appeared. These, compiled by a panel of German authorities on the various topics, contain several sections relevant to intermediates and dyes and are of special interest as they include many references to war-time German patents or patent applications not yet available in this country.

Of general interest, too, is the publication during the year of an American edition, translated by P. W. Vittum, of Fierz David's and Blangey's 'Fundamental Processes of Dye Chemistry,' and of a new, much enlarged edition of 'The Aromatic Diazo-Compounds' by K. H. Saunders. The latter is complementary in many respects to K. Holzach's 'Die Aromatischen Diazoverbindungen' published in 1947 and these two books together give a very comprehensive and up-to-date account of this most important field of organic chemistry.

Output and trade statistics for the dyestuffs industry are available for 1948 and also for the first six months of 1949. According to Mr. G. E. Holden, the Dyestuffs Controller, the output of British dyes was 46,000 tons in 1948 compared with 38,000 tons in 1947 and 20,000 tons in 1938.[1] Production in the United States, however, decreased slightly from 95,000 tons in 1947 to 88,000 tons in 1948.[2] Of the 1948 production, azo dyes accounted for 44%, indigoid and anthraquinone vat dyes for 30% and sulphur dyes for 10%. Detailed figures for some of the more important industrial dyes are also available.[3] Export figures for dyes and organic pigments for the first half of 1949 have been given as: United States 8932 tons (value £7,596,000), United Kingdom 6998 tons (value £5,079,000), and Switzerland 3733 tons (value £5,784,000). The high value of Swiss exports relative to the weight emphasizes the well-known policy of the Swiss firms of concentrating on speciality products.

INTERMEDIATES (D. A. W. Adams, B.Sc., Ph.D.)

The enormous number of patents covering the manufacture of general organic chemicals issued during the year under review, both in this country and in the United States, makes it again necessary to restrict the field to be discussed to that outlined in last year's report. In order to try to make the report more readable, however, an attempt is made this year to separate the publications dealing with general unit operations and improvements in manufacture of well established products from those covering new compounds of particular interest as intermediates for dyestuffs.

Much of the patenting in the United States is by the firms concerned with the production of chemicals, both aliphatic and aromatic, from petroleum ; although much of this field is outside the scope of this review a brief mention must be made here because of the effect of these developments on the essential raw materials for the dyestuffs industry. J. R. Skeen,[4] for instance, has drawn attention to the considerable increase in the consumption of products, particularly β-naphthol and phthalic anhydride, derived from naphthalene ; J. M. Weiss,[5] discussing the increasing shortage of benzene and naphthalene, suggests various ways of overcoming it by use of petroleum chemicals. The shortage of naphthalene is actually being alleviated to some extent in the United States by the manufacture of phthalic anhydride from *o*-xylene or other alkylbenzenes.[6]

Some U.S. patents (probably without British equivalents) of a process-improvement type from firms formerly having technical agreements with German concerns appear to be designed to prevent their processes from becoming generally available in the United States as a result of the publication of German information in BIOS and FIAT reports.

The excellent review of unit operations referred to in the last report (Annual Reports, 1948, 33, 66) has been followed by a second similar review covering essentially the further publications during 1948 and the first half of 1949.[7]

Aliphatic intermediates

Aliphatic chloro- and bromo-compounds

(*a*) *Chlorination of aliphatic hydrocarbons, etc.*—The chlorination of methane using a melt of $KCl–Cu_2Cl_2–CuCl_2$ at 400–475° c. has been studied by E. Gorin, C. M. Fontana and G. A. Kidder.[8] The actual chlorinating agent is $K_2Cu_2Cl_6$ and this is only formed to any extent when the cupric ion concentration exceeds 20%. The main products are MeCl, CH_2Cl_2, $CHCl_3$, and CCl_4, the highest yields of MeCl (77%) being obtained at low conversion rates (9·2%). Because of the difficulty of obtaining pure substances by the direct chlorination of methane, V. Berti and G. Salvi[9] studied the use of sulphuryl chloride with such catalysts as $FeCl_3$, $CuCl_2$, and mixtures of copper and aluminium chlorides. They were unable, however, to obtain selective formation of any desired chlorination product and CCl_4, in particular, could not be obtained by this method.

The chlorination of ethane and also of propane and butane has been examined by E. T. McBee and his co-workers.[10,11] Although ethane can

be made to give mainly ethyl chloride with $CH_2:CHCl$ and some $C_2H_4Cl_2$ and C_2H_4 as by-products, propane and butane give mainly polychlorinated compounds. By passing chlorine and propane continuously into 1 : 2-dichloropropane in presence of actinic light, these compounds are produced in good yield.[12] Longer-chain paraffins can be similarly chlorinated providing the temperature employed is below 150° to prevent chlorinolysis.[13] Dow Chemical Co. find that increased yields of ethyl chloride are obtained in the chlorination of ethane by addition of methane as diluent.[14]

Solvay & Co.[15] effect reaction between acetylene and halogens by passing the gases into a solvent, preferably the halogenated hydrocarbon being formed, in a special apparatus consisting of a synthesis chamber and two dissolving towers. The same firm[16] prepare tetrachloroethane by passing acetylene and chlorine into a boiling mixture of the end-product and another volatile liquid of lower b.p. such as carbon tetrachloride.

(*b*) *Addition of HCl to unsaturated hydrocarbons.*—The main interest in this reaction continues to be the production of vinyl chloride from acetylene and hydrochloric acid in presence of a suitable catalyst. Mercury in various forms is the most usual catalyst: a complex salt of $HgCl_2$ and $AlCl_3$,[17] beads of approximately 5 g. moulded from a mixture of $HgCl_2$ (10%) and hydrated Al_2O_3 (90%),[18] $HgCl_2,3KCl$ on activated carbon,[19] and a complex with vinyl chloride, $CHCl:CH{\cdot}HgCl$, on silica gel[20] have all been proposed. Other catalysts employed are arsenic derivatives such as $CHCl:CH{\cdot}AsH_2$[21] and antimony or bismuth halides.[22]

Alkyl halides are prepared by Pure Oil Co. from olefines and hydrochloric acid in presence of oxyhalides of thorium.[23]

(*c*) *Conversion of alcohols into alkyl halides.*—A. W. Billitzer[24] describes the manufacture of ethyl chloride from ethanol and hydrochloric acid gas in presence of anhydrous calcium chloride at 100° c. The HCl gas is generated from $CaCl_2$ and hydrochloric acid with sulphuric acid, the only waste product being gypsum. N.V. Chemische Fabriek 'Naarden'[25] use a counter-current process for conversion of mono- or poly-hydric alcohols into alkyl halides, the product being removed from one end of a tubular reaction vessel and water from the other; dodecyl bromide is so prepared.

Shell Development Co.[26] effect simultaneous replacement of OH by Cl and direct chlorination by treating monohydric alcohols with HCl and oxygen in presence of a catalyst such as that used in the Deacon process for the manufacture of chlorine, e.g. Al_2O_3 impregnated with a copper halide. Ethanol is thus converted into 1 : 2-dichloroethane.

Aliphatic fluoro-compounds

(*a*) *Addition of HF to unsaturated hydrocarbons, etc.*—Vinyl fluoride is becoming as important as the chloride and several methods for its preparation from acetylene have been recorded during the year. Imperial Chemical Industries Ltd. claim a multiple chromite of mercury and a metal which forms a hydrogenating oxide such as Zn.[27] E. I. Du Pont de Nemours & Co. (hereafter called Du Pont) describe a 2-stage process[28] in which $CHMeF_2$ is prepared from acetylene and hydrofluoric acid in

presence of BF_3 at 0–30° c. and 5–150 lb. per sq. in., and is then heated at 300–600° c. in presence of a dehydrofluorination catalyst or a little oxygen.[29] Allied Chemical and Dye Corporation[30] also make $CHMeF_2$ by passing acetylene and HF into a mixture of fluorosulphonic acid and hydrofluoric acid at 0° c.; at higher temperatures vinyl fluoride is obtained directly.

Du Pont further fluorinate saturated fluorohydrocarbons such as $CHMeF_2$ (to $CMeF_3$) by heating with HF in presence of oxidizing agents such as Co_2O_3 and PbO_2.[31]

(*b*) *Replacement of chlorine by fluorine.*—This well known and widely applicable method of producing fluoro-compounds continues to be studied, and J. H. Brown and W. B. Whalley[32] have investigated the use of the theoretical quantity of HF for replacing one Cl in several simple polychlorohydrocarbons, in the absence of catalysts. CCl_4 gives CCl_3F (63% yield), $CH_2Cl{\cdot}CCl_3$ gives $CH_2Cl{\cdot}CCl_2F$ (80%), $CHCl_2{\cdot}CCl_3$ gives $CHCl_2{\cdot}CCl_2F$, C_3Cl_6 gives a complex mixture, and $CMeCl_3$ gives $CMeCl_2F$ and $CMeClF_2$; $CHMeCl_2$, however, gives only a small yield of mixed products. Imperial Chemical Industries Ltd. carry out similar reactions in presence of stannic chloride.[33] Purdue Research Foundation[34] pump CCl_4 and HF (1 : 5 mol. ratio) continuously into a Ni-lined vessel at 395° c./3000 lb. per sq. in. and vent the gases, obtaining mainly CCl_3F, whilst Du Pont[35] pass CCl_4 or its partly fluorinated derivates with HF over CrF_3 or FeF_3 at 800–950° c. to obtain CF_4.

Harshaw Chemical Co.[36] convert $CH_2Cl{\cdot}CN$ into $CH_2F{\cdot}CN$ by interaction in liquid or vapour phase with HgF_2, CdF_2 or, preferably, AgF, the fluorinating agent being regenerated by treatment with fluorine followed in the case of the last-named catalyst by treatment with methane to convert AgF_2 into AgF.

(*c*) *Electrochemical processes for the production of fluorocarbons.*—The electrolysis of organic compounds in liquid HF, using Ni anodes, Ni, Fe or Cu cathodes, 5–6 v. and current density of approximately 0·02 amp. per sq. cm., has been studied by J. H. Simons and co-workers.[37] Pyridine gives NF_3, C_5F_{12} and 2-fluoropyridine, whilst MeCN gives CF_4, $CF_3{\cdot}CN$, and C_2HF_5. Propionic and butyric acids give CF_4 and C_2F_6 together with C_2HF_5, etc., whereas amyl alcohol and caproic acid give CF_4 and CHF_3 together with C_2F_6. Adipic acid gives a product comprising mainly C_4F_{10}. When hydrocarbons are electrolysed, it is necessary to raise the conductivity of the solution by adding a conducting solvent such as water, methanol, acetic acid or ammonia; under such conditions *n*-octane gives mainly C_8F_{18}.

Nitro-compounds

Nothing really novel is disclosed by the new patents in this field, the processes described being essentially minor modifications of those published previously. In the nitration of olefines in the liquid phase,[38–41] solvents are used by Imperial Chemical Industries Ltd. (dimethyl ether) and by Du Pont (acetic acid, carbon tetrachloride, ether, light petroleum, etc.), the nitrating agent being either N_2O_3, NO with oxygen or air, or N_2O_4 diluted with N_2. Temperatures vary from $<$ 0° to 40–50° c. In

addition to dinitroalkenes, nitrates etc. are formed. Imperial Chemical Industries Ltd.[42] have also investigated a vapour-phase nitration of *iso*butane at 250–280° c. using a vessel of vitreous, ceramic or refractory material; mononitro-paraffins, 2 : 2-dinitropropane and 1 : 2-dinitro*iso*butane are formed. Fluoroethylenes are similarly nitrated by Purdue Research Foundation[43] to give, for example, 1 : 2-difluoro-1 : 2-dinitroethane.

Oxygen-containing compounds: alcohols, aldehydes, ketones and acids

A. Oxidation processes

The oxidation, mainly catalytic, of various aliphatic compounds—hydrocarbons, alcohols, aldehydes, etc.—to give products at a higher state of oxidation continues to receive considerable attention.

(*a*) *Oxidation of saturated aliphatic hydrocarbons.*—The incomplete oxidation of methane with free oxygen to give mixtures of CO and H_2, which can then be used in the synthesis of alcohols, etc., has been investigated by A. Lotteri.[44] Clark Bros.[45] convert saturated aliphatic hydrocarbons (CH_4, C_2H_6, etc.) into, e.g., formaldehyde, by treatment with sulphuric acid at 275–325° c. in presence of a compound (salt) of one or more metals such as Co, Ni, Fe, Cu, or Ag, e.g. $CoSO_4$ and $AgNO_3$. The addition of one or more compounds of Ce, Ru, Pt, Pd or Pb improves the yield.[46]

(*b*) *Oxidation of unsaturated aliphatic hydrocarbons.*—The catalytic oxidation of ethylene to ethylene oxide is still being actively studied and obviously is not straightforward (cf. ANNUAL REPORTS, 1947, **32**, 49). Monsanto Chemical Co.[47] pass ethylene, with or without methane or ethane as diluent, with oxygen over a catalyst comprising silver supported on α-silica containing 5–10% of α-alumina, at 225–350° c. R. S. Aries[48] uses a porous carrier such as Al_2O_3 or SiC coated with a uniform layer of uniformly-sized small particles of Ag–Ag_2O; air containing 3·5% of ethylene is passed over this catalyst at 268° c. with a contact time of 4·4 sec. 89% of the ethylene undergoes conversion and of the product 87% is ethylene oxide. Shell Development Co.[49] extract the products of reaction with a lower aliphatic alcohol which selectively extracts ethylene oxide and poisoning impurities and allows the undissolved portion to be recycled. M. Mitani and H. Kano[50] have studied the formation of ethylene oxide using a silver catalyst activated with acetic acid; conversions of 38% at 345° c. were obtained. Electrolytic (anodic) oxidation of ethylene has been unsuccessfully attempted by M. A. Kalinin and V. V. Stender[51] using Pb and Pt anodes; electrolytic chlorination in 2% HCl using a graphite anode, however, gave 80–85% yields of chlorohydrin.

Using Cu_2O as catalyst at 250–450° c./10 atm., olefines containing $\nless$ 3 C atoms are oxidized with oxygen (deficiency) in presence of a diluent gas to give unsaturated aldehydes. Propylene gives acrolein, whereas but-1- and -2-enes give but-1-en-3-one.[52] The Lubri Zol Corporation[53] also achieve partial oxidation by careful control of time, temperature, ratio of oxidizing agent to reactant, and addition of benzene as diluent; alcohols, aldehydes and ketones are obtained.

The Research Corporation[54] oxidize unsaturated compounds to saturated alcohols, aldehydes, etc. with hydrogen peroxide in an inert, anhydrous solvent in presence of an oxide catalyst such as OsO_4, RuO_4, V_2O_5, Mo_2O_3 or Cr_2O_3. $CH_2{:}CMe_2$ thus gives $OH{\cdot}CMe_2{\cdot}CH_2{\cdot}OH$; $(CH_2{\cdot}CH{:}CH_2)_2$ gives hexane-1 : 2 : 5 : 6-tetrol.

Oxidations in sulphuric acid to give acids is claimed by Emery Industries Ltd.[55] and by British Celanese, Ltd.[56] The former electrolyse an aqueous solution containing 10–15% H_2SO_4 and 15–35% $Cr_2(SO_4)_3$ to give H_2CrO_4 in solution, this solution then being used to oxidize long-chain unsaturated fatty compounds at 50–100° c. British Celanese, Ltd. electrolyse olefines such as propylene in 5% H_2SO_4 to give acids, e.g. propionic acid.

The United States Rubber Co.[57] prepare trichloroacetyl chloride by passing oxygen and chlorine through tetrachloroethylene in presence of organic peroxides such as benzoyl peroxide. Compounds such as $CF_2X{\cdot}CX{:}CXCl$ (X is Cl or F) are similarly treated[58] with oxygen and chlorine in presence of actinic light to give acid chlorides, $CF_2X{\cdot}CXCl{\cdot}COCl$, which can subsequently be converted *via* the amide into the nitrile.

(*c*) *Oxidation of alcohols and alkylene oxides.*—Both liquid-phase and vapour-phase oxidations of alcohols are described. Universal Oil Products Co.[59] treat alcohols with oxygen in presence of manganese acetate below the critical temperature and under sufficient pressure to maintain the liquid state. A fractionating type of column is used and the process is operated continuously. Acetone is so prepared from *iso*propanol. The same firm[60] also use a vapour-phase oxidation in presence of a catalyst comprising copper (60–62%), zinc (35–38%) and lead (2·4–3·2%); the reaction is carried out at 420–500° c./1–100 atm. with an hourly liquid space velocity of approximately 4.

L. G. Farkas and O. Schacter[61] boil primary or secondary alkanols or alkanals in presence of bromine, another oxidizing agent such as chlorine, oxygen or a bromate, and a promoter such as a Cu or Mo compound; aldehydes, ketones, acids, etc. are produced. Ethylene chlorohydrin is oxidized by Du Pont with nitric acid at 60° c. to give chloracetic acid in 84% yield.[62]

The Pennsylvania Salt Manufacturing Co.[63] oxidize alkylene oxides at low temperature with chlorine to form aldehydes with very little formation of chloro-compounds; ethylene oxide, for instance, gives acetaldehyde and its trimer.

(*d*) *Oxidation of aldehydes to acids.*—Usines de Melle[64] oxidize aldehydes with an oxygen-containing gas, containing less oxygen than does air, at 30–60° c. in presence of manganese acetate; the preparation of acetic and propionic acids is claimed. Polymerizable Products Ltd.[65] use multivalent metal salts of unsaturated fatty acids, e.g. a mixture of lead, manganese and cobalt oleates (37·2 : 34·7 : 28·1%), for similar oxidations. H. Dreyfus[66] obtains acid anhydrides by oxidizing aldehydes in presence of copper and cobalt acetates, water being removed continuously by azeotropic distillation with methylene chloride.

The oxidation of crotonaldehyde is described by British Celanese Ltd.

and the Celanese Corporation of America. Using oxygen and a solvent such as acetic acid containing, as catalysts, manganese acetate and potassium permanganate, crotonic acid is obtained in 78% yield.[67] For the vapour-phase oxidation to maleic acid and anhydride they use as catalyst V_2O_5 and MoO_3 and optionally P_2O_5 supported on alumina[68]; the addition of an inert diluent such as steam permits the use of a lower temperature and results in a higher yield.[69]

(*e*) *Oxidation of* cyclo*aliphatic compounds, etc.*—Phillips Petroleum Co.[70] prepare succinic acid by a two-stage oxidation of *cyclo*pentane; in the first stage, a mixture containing *cyclo*pentanol is obtained by air oxidation at 140° c./400 lb. per sq. in. and in the second stage this crude mixture is further oxidized with nitric acid at 65–70° c. A modified continuous process for adipic acid from *cyclo*hexane is described by the Union Oil Co. of California[71]; 50–70% nitric acid, introduced into the middle of a column containing *cyclo*hexane, reacts in the upper part of the column at 100–160° c. to form nitro*cyclo*hexane which is then oxidized in the lower part of the column at 100–130° c. to adipic acid.

Tetrahydrofuran can be made to yield either γ-hydroxyaldehydes or γ-butyrolactone according to the conditions employed. By oxidation at 25–40° c. in presence of a salt of Co, Ni, Mn or Cu, followed by decomposition of the peroxide so formed by heating with aqueous acid or alkali or by controlled hydrogenation, Usines de Melle obtain butan-4-ol-1-al.[72] Imperial Chemical Industries Ltd., however, by oxidation at 100–140° c. in presence of an inert solvent (benzene or acetic acid) and a catalyst such as benzoyl peroxide or a metal salt of a long-chain carboxylic acid, obtain the butyrolactone.[73] The oxidation of furfuraldehyde at 270° c. in presence of a catalyst comprising a mixture of oxides of Mo, Fe and V on an alumina carrier has been studied by E. K. Nielson[74]; 95% conversions were obtained and yields of maleic acid reached 75% or higher.

(*f*) *HBr-catalysed oxidations to give peroxides.*—Shell Development Co. continue to be interested in the production of peroxides from hydrocarbons by oxidation with oxygen in presence of hydrobromic acid gas. Improved results are claimed by initially activating the walls of the reaction vessel (glass or fired silica) by treatment with bromic acid[75] or with nitric acid and/or NO_2.[76]

B. *Reduction processes*

As a means of making oxygen-containing compounds, hydrogenation is much less important than oxidation and only one patent need be mentioned. Usines de Melle[77] describe the preparation of copper catalysts for hydrogenating aldehydes and stress the importance of keeping the temperature low during the reduction of the CuO. Such catalysts give complete conversion of acetone into *iso*propanol at 150° and also complete conversion of crotonaldehyde into *n*-butanol at 100°.

Two patents are concerned with electrolytic reductions: such reduction in dilute sulphuric acid containing ferrous sulphate and/or zinc acetate and quinol is used by British Celanese Ltd.[78] for the conversion of acrolein into allyl alcohol, whilst C. S. Dillon[79] describes the preparation of lactic aldehyde by electrolysis of aqueous solutions of lactic acid.

C. Syntheses involving carbon monoxide

Syntheses involving carbon monoxide, with and without hydrogen (the OXO process), are still receiving attention. Du Pont[80] treat olefines with CO (1 mol.) and H_2 (2–4 mols.) in presence of reducing agents such as Co, Co–Cu, Co–Fe, optionally promoted with ThO_2 or Mn, and optionally in an inert solvent. By working at pressures greater than 300 atm., ketone formation is virtually avoided and the main products are aldehydes. If water is present unsaturated aldehydes are formed ; prolongation of the reaction gives alcohols. At 140–145°/500 atm. ethylene gives a conversion of 33·5% in 0·5 min. into 95·5% EtCHO. Using carbon monoxide and steam at 200–400°/500–1500 atm. and nickel or cobalt carbonyls on active carbon as catalyst, the same firm[81] obtain carboxylic acids as the main products. Using ethylene, steam and carbon monoxide at 100°/850–1000 atm., an acid is obtained which on oxidation with aqueous nitric acid gives essentially succinic acid.[82]

W. H. Groombridge[83] prepares acetic acid in 50% yield by heating methyl chloride, water, carbon monoxide, a metal carbonyl and a little iodine at 330° c./350–450 atm. Imperial Chemical Industries Ltd.,[84] using polyhalogeno-ethanes and carbon monoxide in presence of a Friedel-Crafts catalyst at 70–200° c./50–1000 lb. per sq. in., obtain polyhalogenoacyl halides ; C_2HCl_5 for instance gives a tetrachloropropionyl chloride.

D. Miscellaneous reactions for obtaining oxygen-containing compounds

N.V. de Bataafsche Petroleum Maats.[85] treat compounds of the type $COR{:}CR{\cdot}CR_2$ with alcohols, $CHR'_2{\cdot}OH$ (R is alkyl or alkenyl and R' is H or alkyl), in the vapour phase at 350–450° c. in presence of a mixture of MgO and ZnO to give unsaturated alcohols, $CR_2{:}CR{\cdot}CHR{\cdot}OH$. Thus acrolein and ethanol give allyl alcohol in 71% yield.

Usines de Melle[86] prepare aldehydes by passing formic acid and another organic carboxylic acid in liquid or vapour phase into a mechanically agitated suspension of a decarboxylation catalyst such as an oxide of Mn, Fe, Th or Al, or manganese acetate, in an inert liquid medium ; if formic acid is replaced by other acids, then ketones are similarly formed. Thus acetic acid at 300–330° c. gives acetone in 96–98% yield and 65% conversion, whereas acetic acid and benzoic acid give mainly acetophenone. Unsaturated aldehydes and ketones are made by Standard Oil Development Co.[87] by interaction of two mols. of the same or one each of two different aldehydes or ketones at 350–450° c. under pressure in presence of hydrogen and a catalyst comprising a mixture of oxides of a Group II and Group V metal. Methyl ethyl ketone is thus converted into a methylheptanone.

Aliphatic carboxylic acids are prepared by the Gulf Research and Development Co.[88] by a rather unusual reaction in which olefines are heated with sulphur at 140–350° c. to give S-containing compounds, $C_nH_{2n-4}S_3$, which are then hydrolysed with excess of aqueous caustic soda. Di-*iso*butene, for example, gives, *via* a compound $C_8H_{12}S_3$, 3 : 3-dimethylvaleric acid in 80% yield. Also of interest is Du Pont's

method[89] of preparing difluoroacetic acid by hydrolysis of 2 : 4 : 6-tris-(difluoromethyl)-*s*-triazine at 50–150° C. in presence of a base or acid and optionally in a water-immiscible solvent such as dioxan.

Amines

The effect of operating variables on the production of methylamine from methanol and ammonia has been studied by R. S. Egly and E. F. Smith,[90] the optimum conditions being protected by a patent issued to Commercial Solvents Corpoation.[91] M. Simonetta[92] similarly studied the preparation of *iso*propylamine by hydrogenation of acetoxime.

In the hydrogenation of long-chain cyanides such as stearonitrile, Emery Industries Inc.[93] obtain increased yields of primary amine by the well-known technique of adding 50–200% by weight of the corresponding secondary amine. Du Pont[94] use titanium hydride as catalyst in the reduction of nitriles, e.g. adiponitrile, and nitro-compounds.

Cyanides

There has been very considerable publication during the year, particularly in the form of patents assigned to the Socony-Vacuum Oil Co., Inc.,[95] on the direct production of cyanides from hydrocarbons and ammonia. Saturated and unsaturated aliphatic and *cyclo*aliphatic hydrocarbons, and aromatic hydrocarbons have all been employed. The preferred catalyst is MoO_3 on activated alumina, although tungsten oxides and V_2O_5 are also used. Conversions in general are small and it remains to be seen whether economically successful processes can be operated. Ethylene and propylene give 25% and 32% conversions, respectively, into methyl cyanide; *n*-propane and *n*-butane give lower (2·4–5·2%) conversions. Methyl*cyclo*hexene gives methyl cyanide together with some benzyl cyanide and methyl*cyclo*hexane gives cyanobenzene; in these cases, the reaction is considered to proceed by ring-opening, replacement of H by N, and subsequent dehydrogenation and ring-closure. Aromatic compounds such as toluene give cyanobenzene, the conversion being 6–7%.

The Sinclair Refining Co.[96] claim cobalt with or without a metallic promoter and supported on TiO_2 as an improved catalyst for this reaction; Phillips Petroleum[97] use a granular synthetic activated alumina.

R. S. Hanmer and S. Swann[98] show that methyl cyanide is the main product of the interaction of acetylene with ammonia in molten mixtures of zinc and alkali chlorides at temperatures above 430° C. Du Pont heat aldehydes with ammonia in presence of metallic cobalt[99] or copper–zinc[100] catalysts at 300–350° C., obtaining cyanides; EtCHO gives a 77% yield of ethyl cyanide with 3 : 5-dimethyl-2-ethylpyridine as the main by-product.

Benzenoid intermediates

Alkylation of hydrocarbons, phenols, etc.

The nuclear alkylation of aromatic hydrocarbons, phenols, etc., with olefines continues to receive attention but recent patents only cover minor modifications of the general reaction. Universal Oil Products Co. protect the use of a catalyst made by calcining $Cu_3(PO_4)_2$, $3H_2O$ at 300–320° C.[101] and also the use of an $AlCl_3$–hydrocarbon complex made by treating $AlCl_3$ with, for example, ethylene in presence of HCl.[102]

Compagnie Française de Raffinage[103] partly convert the olefine (C_2H_4) into an alkyl halide before reaction with the aromatic hydrocarbon, by treatment with a hydrogen halide in presence of $AlCl_3$ or Al chips.

Imperial Chemical Industries Ltd.[104] prepare *p-tert.*-butylphenol by passing a mixture of CH_2:CMe_2, *n*-butane and *n*-butene into phenol and a little concentrated H_2SO_4 at 60–70° c. and then heating to 150° c. to effect isomerization. *o*-Alkylation of phenols is effected by Universal Oil Products Co.[105] by using a carboxylic acid as catalyst, e.g. $CCl_3{\cdot}CO_2H$ or $H_2C_2O_4$.

Halogenation

The continuous liquid-phase chlorination of benzene in presence of iron filings, using the desired reaction product as reacting medium, is described by Solvay & Co.[106] California Research Corpn.[107] claim the use of an active metal silicate containing lattice water, interlattice adsorbed water but no hydrous water; monochlorinated compounds are formed almost exclusively.

In the addition-chlorination of benzene to the hexachloride ($C_6H_6Cl_6$), A. P. H. Dupine[108] uses moist chlorine in presence of an oxidizing catalyst such as NO, NO_2, NOCl, or NO_2Cl. An improved process for the side-chain chlorination of xylene is claimed by Du Pont[109] in which, after about 50% chlorination has occurred, the chlorine stream is mixed with 5% of air; P_2O_5 is also added to prevent polymerization due to metals.

H. Nordt of the I.G. Farbenindustrie[110] has found that when phenol is chlorinated in the vapour-phase at 250° c., the proportion of *o*-isomer is much higher than in the liquid-phase chlorination at 40–50° c.; as the *p*-isomer is the more important product, however, there would appear to be no practical application of this.

In the chlorination of phthalic anhydride in presence of $FeCl_3$, B. F. Goodrich Co.[111] prevent the blocking of condensers by sublimed material by addition of a chlorinated hydrocarbon of b.p. 60–275° c., e.g. *o*-dichlorobenzene or $C_2H_2Cl_2$. The same firm describe[112] a vapour-phase chlorination at 340–360° c. using $ThCl_4$ or $CuCl_2$ as catalyst. Niagara Alkali Co.[113] use molybdenum chlorides as catalysts for the preparation of tetrachlorophthalic anhydride. A 91·5% yield of *p*-bromophenol is obtained by Colgate-Palmolive-Peet Co.[114] by bromination of phenol in liquid SO_2 at − 8° c. Minnesota Mining and Manufacturing Co.[115] fluorinate benzene with fluorine in pyridine at − 15° c., to give fluorobenzene and some higher-boiling compounds.

Nitration

Little new has appeared on the technique of nitration. The Biazzi continuous process for the nitration of glycerol, benzene, toluene, cresols, etc., is described by J. C. Smith.[116]

The nitration of trichloroacet-*o*-toluidides has been studied by A. McGookin[117]; substitution occurs largely in the *o*- and *p*-positions in spite of the expected influence of the chlorine atoms. American Cyanamid Co.[118] describe a modified process for the nitration of acylarylides. As an example, *o*-toluidine is converted into the *p*-toluenesulphonyl derivative by treatment with the acid chloride in chlorobenzene in

presence of water and caustic soda; after neutralization, the slurry is heated to 50° C. to cause dissolution of the product in the chlorobenzene and allow the aqueous layer to be separated. A surface-active agent is added, nitration is carried out at 50° C. with aqueous nitric acid and after removal of the solvent the product is hydrolysed with sulphuric acid to give 5-nitro-*o*-toluidine.

Oxidation

The Socony-Vacuum Oil Co. have continued their study of the catalytic oxidation of benzene to phenol, and two patents[119] are concerned with the use of organic promoters characterized by being better H-donors than benzene itself, e.g. *cyclo*hexane, cracked gasoline, ethers, etc. In another variation,[120] porous adsorbent V_2O_5 catalyst is used at 316° C., the catalyst being in contact for less than 60 min. (5 min.) and then being continuously removed and stripped with a solvent to remove the phenol. The yield by this procedure is 1·9% compared with about 0·3% by previous methods. Naphthalene can be oxidized similarly to naphthols. A marked increase in efficiency would appear to be necessary before the process can compete with the conventional methods now in operation.

The production of phthalic anhydride from *o*-xylene obtained from petroleum sources is still engaging the attention of California Research Corpn.,[121,122] the preferred catalyst being vanadium or an alloy having an indigenous coating of vanadium oxide. They describe a 5-stage process starting from petroleum fractions containing 6–12 C atoms, involving intermediate aromatization and conversion to suitable mixtures of alkylbenzenes.[123]

In the oxidation of ethylbenzene to acetophenone in presence of a chromium oxide catalyst, Monsanto Chemical Co.[124] have found that the presence of α-hydroxyethylbenzene seriously retards the reaction; once the initial reaction has occurred, however, it may be deliberately added. Yields of acetophenone of 44% are claimed. The same company[125] oxidize *p*-ethylbenzyl acetate to *p*-acetylbenzyl acetate in the liquid-phase in presence of a chromium oxide and chalk. Alkylbenzenes in which at least one alkyl group has an α-*tert.*-C atom are oxidized at p_H 7–11 in the liquid-phase to give peroxides and hydroperoxides.[126]

When benzene or alkylbenzenes are heated at 50° C. with 50% nitric acid containing 6·5–7% of mercuric nitrate on a counter-current principle, nitrophenols are formed of which 85–90% are dinitro-compounds.[127]

Amino-compounds

The production of amines both by reduction of nitro-compounds and by ammonolysis continues to receive attention and improvements in techniques are still being recorded.

(*a*) *Reduction processes.*—Several publications, principally by the Standard Oil Development Co., are concerned with the development during the war of processes for the xylidines, required for addition to aviation petrol, by catalytic reduction of the nitroxylenes.[128] Both Ni or Ni–Cu on an inert carrier and Mo sulphides on a charcoal carrier were used as hydrogenation catalysts,[129] the latter being constantly reactivated with H_2S[130] or with CS_2.[131] The optimum temperature

(149–232° c.) was maintained by continuous addition of water. Shell Development Co.[132] describe a similar process.

The Institute of Physical and Chemical Research (Japan)[133] describe a process for *o*-4-xylidine in which *p*-nitrotoluene is treated with bis-chloromethyl ether in sulphuric acid and the product is then catalytically hydrogenated. The separation of various xylidines from the mixture obtained by reduction of crude nitroxylene is still being studied. A. A. Spryskov[134] treats the crude mixture in a solvent with hydrochloric acid to precipitate the *m*-4-xylidine as hydrochloride (90% purity) and then adds sulphuric acid and sodium sulphate to the filtrate to precipitate the *p*-xylidine as sulphate. The Anglo-Iranian Oil Co., Ltd.[135] describe processes for recovery of *o*-4-xylidine from the filtrates from the separation of *m*-4- and crude *p*-xylidines, and also of *m*-2-xylidine from the re-crystallization of the crude *p*-xylidine. In both cases the liquors are basified and the oil is fractionally distilled, the crude products then being purified by, respectively, crystallization and conversion to the formyl-compounds. These processes should be compared with those adopted by the I.G. Farbenindustrie as described in BIOS reports (cf. ANNUAL REPORTS, 1947, **32**, 51).

The Boyle-Midway Co.[136] recover *m*-phenylenediamine from the waste eutectic of 1-chloro-2 : 4- and 1-chloro-2 : 6-dinitrobenzenes by hydrogenation in presence of Raney nickel and sufficient alkali to neutralize the hydrochloric acid generated during the reduction; the NO_2 groups are reduced first and the alkali is preferably added when this stage is complete. Yields of 84% are claimed.

Partial reductions of dinitro-compounds figure in two publications. G. D. Parkes and A. C. Farthing[137] reduce trinitrotoluene to 2 : 6-dinitro-*p*-toluidine by passing H_2S into a solution in dioxan containing a little ammonia; 6-chloro-2 : 4-dinitrophenol is reduced to 6-chloro-4-nitro-2-aminophenol (by General Aniline and Film Corpn.)[138] by treatment with Na_2S_2 in presence of magnesium chloride and lime, firstly at 30–35° and finally at 80° c.; the product is isolated as calcium salt.

(*b*) *Ammonolysis processes.*—In the ammonolysis of chlorobenzene in presence of a cuprous catalyst, Dow Chemical Co.[139] use a continuous process in which the reactants are first heated in a heating-zone and then passed through the reactor with no external heating at rates of flow well below those which cause emulsification; it is claimed that under these conditions excessive corrosion is avoided. Catalyst is conserved by recycling part of the aqueous layer from the reaction mixture.[140] Standard Oil Development Co. of Ohio[141] obtain *N*-methylaniline in 93% yield from chlorobenzene and methylamine containing cuprous chloride at 215–225° c.; the methylamine solution (or ammonia for the similar preparation of aniline) may initially be saturated with sodium chloride.[142] In the preparation of diphenylamine from aniline in presence of caustic soda, Dow Chemical Co.[143] add a little of a potassium salt (e.g. KCl) and use chlorobenzene for the azeotropic removal of water. Timbrol, Ltd.[144] avoid the use of acidic catalysts in preparing diarylamines by the condensation of phenols with arylamines by using one of the reactants as its Al or Mg compound. Aluminium foil, for example, is dissolved in *p*-cresol,

and the mixture is heated with aniline at 320–330° C. for 5 hr. to give a 19% conversion into 4-methyldiphenylamine.

J. S. F. Turski[145] has improved the process for introducing NH_2 into aromatic compounds by means of hydroxylamine in sulphuric acid by using a catalyst which is wholly dissolved in the acid, e.g. $(VO)_2(SO_4)_3$. The process is widely applicable and many examples are given of its use in the benzene, naphthalene and anthraquinone fields. The position of the entering NH_2-group is such that in some cases the products obtained are those not generally formed in more conventional processes. Benzene gives a 70% yield of metanilic acid free from *o*- and *p*-isomers; with nitrobenzene and dimethylaniline, however, the products are mainly the *o*-substituted derivatives, *o*-nitroaniline and *o*-aminodimethylaniline, respectively. Benzophenone gives mainly the *m*-amino-derivative and azobenzene gives a 85% yield of mixed aminoazobenzenes. Naphthalene gives a mixture of various naphthylamine sulphonic acids, anthraquinone gives 2-aminoanthraquinone, whereas various vat dyes are obtained from dibenzanthrone, etc.

Miscellaneous reactions

Merck & Co., Inc.[146] describe an improvement of the Wolff-Kishner reaction for the reduction of CO-compounds to CH_2-compounds by heating at 170–210° C. with hydrazine hydrate in presence of an alkali metal hydroxide and a high-boiling solvent such as polyethylene glycol. Vanillin so treated and then re-methylated gives 3 : 4-dimethoxytoluene.

In the catalytic acylation of phenyl alkyl ethers dealkylation is prevented by using as catalyst either an acid such as *p*-toluenesulphonic acid, fluosulphonic acid, fluophosphoric acid, etc.,[147] or fuller's earth, Super-Filtrol, etc.[148]

An alternative to the benzidine-type reduction of *o*-nitrophenoxyacetic acid for the preparation of 4 : 4′-diamino-3 : 3′-biscarboxymethoxydiphenyl is described by General Aniline & Film Corpn.[149]; dianisidine is dealkylated with $AlCl_3$ and the resulting dihydroxy-compound, after protection of the NH_2 groups by acylation, is treated with chloroacetic acid in presence of caustic soda, the protecting group being finally removed.

New intermediates for use in dyestuffs

A number of the dyes described later in the section on Azo Dyes have as components new intermediates; where these are of a new type or where their preparation includes points of interest, they are also considered here.

Aminobenzenesulphonyl fluorides, of use in azoic dyes (p. 278), are made by American Cyanamid Co.[150] by heating an acylaminobenzenesulphonyl chloride with aqueous potassium fluoride at 135–140° C.; *p*-aminobenzenesulphonyl fluoride and 2-aminotoluene-4-sulphonyl fluoride are examples. Other fluorine containing intermediates for cellulose acetate dyes are described by Eastman Kodak Co.[151]; diazo-components of the type of 2-fluoro-4-nitroaniline are made from 1 : 2-difluoro-4-nitrobenzene by heating with ammonia at 150–160° C.; coupling components of the type of 1 : 4 : 2-$SCF_3{\cdot}C_6H_3(NH{\cdot}CO{\cdot}CF_3){\cdot}N([CH_2]_2{\cdot}OH)_2$ are made by nitrating *p*-$SCF_3{\cdot}C_6H_4{\cdot}NH{\cdot}CO{\cdot}CF_3$, reducing, and treating with ethylene oxide. Other diazo-components for cellulose acetate dyes made by the

same firm[152] are of the type $p\text{-}NH_2\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2\cdot NMe_2$, made by condensing $p\text{-}NO_2\cdot C_6H_4\cdot NH\cdot CO\cdot CH_2Cl$ with dimethylamine and then catalytically reducing the NO_2-group. 2-Chloro-5-nitro-*p*-phenylenediamine, used by Manufactures de Produits Chimiques du Nord Etablissements Kuhlmann in cellulose acetate dyes (*see* p. 280), is made by reducing 2-chloro-4-nitroaniline, diacetylating the diamine, nitrating, and finally hydrolysing the protecting acetyl groups.[153]

Parke Davis condense *p*-acetamidophenol with paraform and diethylamine in ethanol and then hydrolyse the acetyl group, obtaining 4 : 1 : 2-$NH_2\cdot C_6H_3(OH)\cdot CH_2\cdot NEt_2$.[154] The temporarily solubilized amines referred to on p. 278, e.g. $p\text{-}SO_3Na\cdot NH\cdot C_6H_4\cdot NMe\cdot SO_3Na$, are made by Francolor by treating $p\text{-}NH_2\cdot C_6H_4\cdot NHMe$ with $Cl\cdot[CH_2]_2\cdot O\cdot SO_3H$ in presence of pyridine, followed by neutralization.[155]

The Society of Chemical Industry in Basle[156] prepare *m*-diamines containing a sulphone or sulphonamide group by oxidizing, e.g. 2 : 4-dinitrophenyl methyl sulphide (I), to the sulphone with hydrogen peroxide and then reducing with iron; (I) is made either from 1-chloro-2 : 4-dinitrobenzene *via* the disulphide or by treating 2 : 4-dinitrothiophenol with chloroacetic acid and decarboxylating.

Polynuclear and heterocyclic intermediates

Naphthalene intermediates

There appears to be a revival of interest in naphthalene derivatives and the preparation of a number of new intermediates is described; others are cited in dyestuffs patents.

Peter Spence & Sons[157] obtain 2-methylnaphthalene free from 1-methylnaphthalene by heating naphthalene with dimethyl ether at 200–700° c. (450° c.) in presence of an alumina–silica catalyst. 1 : 2-Dihydronaphthalene is prepared by Koppers Co., Inc.[158] by dehydrating 1 : 2 : 3 : 4-tetrahydro-l-naphthol or a mixture with 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene (obtained by air oxidation of tetrahydronaphthalene) in presence of Al_2O_3 or Al_2O_3–SiO_2 catalysts, whilst the 1 : 4-dihydro-compound is obtained by Du Pont[159] by reducing naphthalene with an alkali metal in a tertiary alcohol such as *tert*.-butanol. 1 : 2 : 3 : 4-Tetrahydronaphthalene-5- and -6-sulphonyl chlorides are used by Geigy Co. for making intermediates for wool dyes (*see* p. 268).[160]

It is well known that hydrogenation of naphthols, etc. can give either the *ac*.- or *ar*.-derivatives according to the conditions employed. The hydrogenation of *β*-naphthol in presence of a copper chromite catalyst has been shown[161] to give mainly the *ac*.-tetrahydro-derivative, whereas Raney nickel in presence of alkalis is claimed by Shering Corpn.[162] to give mainly *ar*.-derivatives in the case of 1-hydroxy-2-naphthoic acid, 2-hydroxy-3-naphthoic acid and *α*-naphthylamine.

The bromination of 1 : 5-dihydroxynaphthalene (I) and its mono- (II) and di-methyl ethers (III) has been studied by R. Bergmann.[163] (I) gives the 2 : 6-dibromo-derivative in both acetic acid and carbon tetrachloride, (III) gives the 2 : 6-derivative in acetic acid but the 5 : 8-derivative in CCl_4, whereas mixtures are formed from (II).

J. R. Geigy A.-G.[164] describe the manufacture of 4-halogenomethyl

derivatives of 1 : 8-naphthasultone by heating the naphthasultone e.g. with paraformaldehyde in acetic acid saturated with dry HCl gas and in presence of $ZnCl_2$. The halogenomethyl group can be converted into Me, $CH_2{\cdot}OH$, $CH_2{\cdot}SO_3Na$, $CH_2{\cdot}SO_2{\cdot}C_6H_4Me$, CH_2Ph, etc. by known methods and the resulting compounds hydrolysed to the corresponding substituted 1-naphthol-8-sulphonic acids. Using an acid chloride in an inert solvent such as trichlorobenzene in presence of $AlCl_3$, corresponding 4-acyl-derivatives of 1 : 8-naphthasultone are obtained.[165]

Various methods are known for the replacement of a diazo-group by H and two variations are described by the I.G. Farbenindustrie[166] in the preparation of 2-naphthol-4-sulphonic acid from 1-diazo-2-naphthol-4-sulphonic acid; they employ either glucose or metal salts such as ferrous chloride and stannous chloride.

H. H. Hodgson and D. Bailey[167] have studied the separation of 2- and 4-nitro-1-naphthylamines formed when α-acetnaphthalide is nitrated and then hydrolysed. American Cyanamid Co.[168] describe a variation of the usual method for effecting the rearrangement of sodium naphthionate to 1-naphthylamine-2-sulphonic acid in which the reaction is carried out, in an autoclave, in chlorobenzene at 175–200° C. with azeotropic removal of any water (of crystallization) present in the naphthionate. Nitration of 1-acetnaphthalide-3-sulphonic acid has been shown by I.G. Farbenindustrie[169] to give 30% of the 5-, 10% of the 2- and 18% of the 8-nitro-compounds.

Several of the aminonaphtholsulphonic acids that are obtained with difficulty have been prepared by methods involving the nitration of esters of various naphtholsulphonic acids (followed by reduction), or the sulphonation of aminonaphthols. E. Messmer[170] of the I.G. Farbenindustrie has studied the nitration of various naphthol esters. 1-Benzoyloxynaphthalene-4-sulphonic acid gives 60% of the 5-nitro-compound and 35% of the 8-nitro-compound, the 2 : 4-isomer gives mainly the 5-nitro-compound, and 2-benzoyloxynaphthalene-3 : 6-disulphonic acid gives the 8-nitro-compound. Using the carbomethoxy derivative of 2-naphthol-4-sulphonic acid, J. R. Geigy A.-G. obtain a mixture of the 5- and 8-nitro-compounds; this, on reduction, gives the corresponding aminonaphtholsulphonic acids, the 1 : 6 : 8-isomer being isolated as the sparingly soluble sodium salt and the 1 : 7 : 5-isomer precipitated from the filtrate by acidification.

Sulphonation of 2-amino-5-naphthol with aqueous sulphuric acid gives a mixture of approximately equal parts of the 6- and 8-sulphonic acids; separation is effected by means of the relatively insoluble magnesium salt of the 6-isomer.[172] 1-Amino-7-naphthol sulphonated similarly has been shown by the I.G. to give the 3-sulphonic acid and not the 4-sulphonic acid as stated in the early literature. The 4-acid can be obtained by baking the sulphate of 1-amino-7-naphthol and is also formed by Bücherer amination of 1 : 7-dihydroxynaphthalene-4-sulphonic acid.[173]

In the Bücherer condensation of 2 : 5-dihydroxynaphthalene-7-sulphonic acid with 4 : 4′-diaminobenzanilide, S. Peterson and H. Klemer[174] have found that it is only the NH_2 in the *p*-phenylenediamine ring which undergoes reaction. The benzoxazolone from 1-amino-5 : 6 : 7 : 8-tetrahydro-2-naphthol has been nitrated, chlorinated, etc. by

General Aniline & Film Corpn.,[175] the substituent entering in each case the 4-position of the naphthalene ring.

Imperial Chemical Industries Ltd. are studying the aminohydroxy-naphthoic acids analogous to the important aminonaphtholsulphonic acids. Thus, W. F. Beech and N. Legg[176] describe the preparation of 6-amino-4-hydroxy-2-naphthoic acid, the analogue of γ acid, by nitrating 4-keto-1 : 2 : 3 : 4-tetrahydro-2-naphthoic acid to give the 6-nitro-compound, followed by bromination, dehydrobromination, and subsequent reduction of the nitro group.

Anthraquinone and other polynuclear intermediates

The purification of anthracene from mixtures containing carbazole and phenanthrene continues to receive attention. Koppers Co. Inc.[177] hydrogenate the mixture in presence of a metallic sulphide catalyst to convert the anthracene into 9 : 10-dihydroanthracene which can then be separated from the other components by distillation and finally dehydrogenated. Imperial Chemical Industries Ltd.[178] effect purification by not less than two crystallizations from *cyclo*hexylamine with recycling of liquors.

V. V. Kozlov[179] has shown that treatment of anthraquinone with excess (30 mols.) of chlorosulphonic acid gives mainly the 2-sulphonyl chloride; addition of mercury has no effect on the orientation. Allied Chemical and Dye Corporation[180] employ ammonium arsenate as catalyst in the conversion of anthraquinone sulphonic acids into aminoanthraquinones, this being essentially the method used by I.G. Farbenindustrie for the manufacture e.g. of 2 : 6-diaminoanthraquinone.[181]

3-Acyl*meso*benzanthrones are prepared by Imperial Chemical Industries Ltd.[182] by heating methyleneanthrone with an acylacetylene in glacial acetic acid; CBz ⋮ CH for example gives 3-benzoyl*meso*benzanthrone. In the preparation of *iso*dibenzanthrone by fusing dibenzanthronyl sulphides or selenides, the use of a sodium alkoxide in an alcohol of <6C is claimed by American Cyanamid Co.[183] to give a product of higher purity than does the conventional use of caustic potash in ethanol.

Heterocyclic compounds

Derivatives of furan continue to receive attention, particularly by Imperial Chemical Industries Ltd., who have several patents dealing with hydrogenation of furfuraldehyde to furfuryl alcohol,[184] and its tetrahydro-derivative,[185] and of 2 : 5-dialkoxy-2 : 5-dihydrofurans to the tetrahydro-compounds,[186] using a Ni or Co foraminate catalyst. The same firm also oxidize furoin to furil with oxygen in presence of a Co- or Cu-acetate, benzoate, etc.[187] Du Pont chlorinate furan either in an inert solvent ($CHCl_3$, CCl_4)[188] or in the vapour-phase,[189] whereas Distillers Co.[190] chlorinate tetrahydrofuran in glacial acetic acid, obtaining 3 : 4-dichloro- and 3-chloro-4-acetoxy-tetrahydrofurans.

Several firms appear to be interested in the manufacture of carbazole from *o*-aminodiphenyl; Monsanto Chemical Co.[191] oxidize at 330–375° C. in presence of $\not>$ 0·8% of a crystalline alumina or graphite, or a metal salt such as manganese benzoate, sodium chromate or a nitrate of Al, Cu, Co, or Fe; Reilly Tar & Chemical Co.[192] operate at 500–800° C. in presence of

SiO_2 or at 450–600° c. in presence of V_2O_5 or tungstic acid. General Aniline & Film Corpn.[193] remove *o*-aminodiphenyl, remaining in the carbazole, as sulphate by treating the crude product in chlorobenzene with aqueous sulphuric acid.

In the carbonation of 2-hydroxycarbazole, General Aniline & Film Corpn.[194] separate the required 3-carboxylic acid (for Naphtol AS.LB), from the crude mixture containing also the 2 : 1-isomer as the sparingly soluble potassium salt, this method being essentially that disclosed previously in BIOS information. The use by the same firm[195] of acetic acid as diluent in the ring-closure of *N*-acetyl-*N*-arylanthranilic acids to *N*-aryl-2 : 4-diketotetrahydroquinolines also parallels the German procedure.

I.G. Farbenindustrie have developed a process for 1-phenyl-3-methyl-5-pyrazolone and its derivatives from diketen.[196] The normal condensation of phenylhydrazine with diketen in solvents gives the isomeric 1-phenyl-5-methyl-3-pyrazolone, but by first treating diketen with aqueous ammonia and then condensing the resulting acetoacetamide with phenylhydrazine hydrochloride, ring-closure takes place with loss of NH_4Cl and formation of the desired 5-pyrazolone.

Other N-containing ring-systems seem to be receiving attention as dyestuff intermediates. Eastman Kodak Co., for instance, use various 1-alkylbenztriazoles[197] and 3 : 4-dihydroxytetrahydroquinolines[198] as coupling components (*see* p. 279), as well as 4 : 5-trimethylenebenzmorpholines (I)[199] and 3 : 5-diketotetrahydro-1-thia-2 : 4-diazine 1 : 1-dioxide (II).[200] (I) are made by heating benzmorpholines with 1 : 3-dibromopropane at 180–200° c.; (II) is made by heating $SO_2Cl{\cdot}CH_2{\cdot}CO_2H$ with urea, followed by esterification and ring-closure with sodium ethoxide. American Cyanamid Co. use 5-hydroxybenziminazoles[201] and also 4 : 6-diamino-1′ : 2′ : 4′-triazolo-3′ : 4′-2 : 3-triazines,[202] the latter being made by condensing 3-amino-1 : 2 : 4-triazole with dicyanodiamide. 5-Amino-2-aryl-2 : 1 : 3-benztriazoles (*see* p. 275) and 7-aminoindazole and its derivatives (*see* p. 278) also figure as dyestuff intermediates.

References

1 *Chem. Tr. J.*, 1949, **124**, 646
2 Ibid., 736
3 Ibid., **125**, 32
4 *Chem. Engng. News*, 1948, **26**, 2555
5 Ibid., 1949, **27**, 972
6 Skeen, J. R., *Chem. Engng. News*, 1948, **26**, 2958
7 *Ind. Eng. Chem.*, 1949, **41**, 1821
8 Ibid., 1948, **40**, 2128
9 *Riv. Combust.*, 1947, **1**, 64
10 McBee, E. T., Hass, H. B., Burt, W. E. and Neher, C. M., *Ind. Eng. Chem.*, 1949, **41**, 799
11 McBee, E. T. and Devaney, L. W., ibid., 803
12 Purdue Research Foundation, U.S.P. 2,473,161
13 Idem, U.S.P. 2,473,162
14 U.S.P. 2,453,691
15 B.P. 604,384
16 B.P. 606,035
17 Monsanto Chem. Co., U.S.P. 2,446,123
18 Solvay & Co., B.P. 611,915
19 B. F. Goodrich Co., B.P. 609,225

[20] Idem, B.P. 617,335 and U.S.P. 2,436,711
[21] Idem, U.S.P. 2,436,710
[22] Shell Development Co., B.P. 603,099
[23] U.S.P. 2,453,779
[24] *J. Aust. chem. Inst.*, 1948, **15**, 261
[25] B.P. 610,843
[26] U.S.P. 2,442,285
[27] B.P. 603,855
[28] B.P. 619,394–5
[29] U.S.P. 2,442,993
[30] U.S.P. 2,462,359
[31] U.S.P. 2,436,143
[32] *J. Soc. chem. Ind.*, 1948, **67**, 331
[33] B.P. 608,111
[34] U.S.P. 2,443,630
[35] U.S.P. 2,458,551
[36] U.S.P. 2,442,290
[37] *J. electrochem. Soc.*, 1949, **95**, 47
[38] B.P. 613,853
[39] B.P. 608,758
[40] B.P. 609,022
[41] B.P. 603,344
[42] B.P. 606,898
[43] U.S.P. 2,447,504
[44] *Riv. Combust.*, 1947, **1**, 19
[45] B.P. 606,554
[46] B.P. 606,967
[47] U.S.P. 2,458,266
[48] U.S.P. 2,477,435
[49] U.S.P. 2,437,930
[50] *Mem. Faculty Eng. Hokkaido Univ.*, 1947, **8**, 75
[51] *J. appl. Chem., U.S.S.R.*, 1946, **19**, 1045
[52] Shell Development Co., U.S.P. 2,451,485
[53] U.S.P. 2,475,605
[54] U.S.P. 2,437,648
[55] B.P. 604,281
[56] B.P. 609,594
[57] U.S.P. 2,472,946
[58] U.S.P. 2,456,768
[59] U.S.P. 2,456,683
[60] B.P. 610,397
[61] U.S.P. 2,444,924
[62] U.S.P. 2,455,405
[63] U.S.P. 2,435,460
[64] B.P. 603,175
[65] U.S.P. 2,456,549
[66] B.P. 604,269
[67] B.P. 612,346
[68] B.P. 613,775
[69] U.S.P. 2,462,938
[70] U.S.P. 2,452,741
[71] U.S.P. 2,459,090
[72] B.P. 614,392
[73] B.P. 608,539
[74] *Ind. Eng. Chem.*, 1949, **41**, 365
[75] U.S.P. 2,434,888
[76] U.S.P. 2,451,869
[77] B.P. 605,707
[78] B.P. 610,613
[79] B.P. 611,674
[80] B.P. 614,010, U.S.P. 2,437,600
[81] U.S.P. 2,448,375

[82] U.S.P. 2,436,269
[83] B.P. 621,520
[84] B.P. 604,579
[85] B.P. 619,014
[86] B.P. 615,543
[87] B.P. 610,752
[88] U.S.P. 2,470,876
[89] U.S.P. 2,442,995
[90] *Chem. Engng. Progr.*, 1948, **44**, 387
[91] U.S.P. 2,456,599
[92] *Chim. e. Industr.*, 1947, **29**, 267
[93] B.P. 612,712
[94] B.P. 603,825
[95] U.S.P. 2,450,632, 2,450,636–42, 2,450,676–8 and 2,463,456–7
[96] U.S.P. 2,468,522
[97] U.S.P. 2,432,532
[98] *Ind. Eng. Chem.*, 1949, **41**, 325
[99] U.S.P. 2,443,420
[100] U.S.P. 2,452,187
[101] U.S.P. 2,442,878
[102] B.P. 615,624
[103] B.P. 615,566
[104] B.P. 616,829
[105] U.S.P. 2,477,091
[106] B.P. 605,693
[107] U.S.P. 2,473,990
[108] B.P. 613,519
[109] U.S.P. 2,446,430
[110] FIAT Review of German Science, 'Preparative Organic Chemistry,' Pt. I, p. 268
[111] U.S.P. 2,460,564
[112] U.S.P. 2,460,565
[113] U.S.P. 2,429,885
[114] U.S.P. 2,452,154
[115] U.S.P. 2,447,717
[116] *Chem. Industr.*, 1948, **62**, 929
[117] *J. Soc. chem. Ind.*, 1948, **67**, 23
[118] U.S.P. 2,459,002
[119] U.S.P. 2,444,233–4
[120] U.S.P. 2,456,597
[121] U.S.P. 2,438,369
[122] U.S.P. 2,474,001
[123] U.S.P. 2,474,002
[124] U.S.P. 2,444,816
[125] U.S.P. 2,439,204
[126] Distillers Co. Ltd., B.P. 610,293
[127] Allied Chemical & Dye Corpn., U.S.P. 2,455,322
[128] De Largey, R. J., Okie, J.P. and Roberts, L. M., *Chem. Engng.*, 1948, **55** (No. 10), 124
[129] *Ind. Eng. Chem.*, 1948, **40**, 1530
[130] U.S.P. 2,430,087
[131] B.P. 602,880
[132] U.S.P. 2,458,214
[133] Jap. Patent 162,726
[134] *J. appl. Chem., U.S.S.R.*, 1948, **21**, 156
[135] B.P. 619,873
[136] U.S.P. 2,464,044
[137] *J. chem. Soc.*, 1948, 1275
[138] U.S.P. 2,464,194
[139] U.S.P. 2,432,551
[140] U.S.P. 2,432,552
[141] U.S.P. 2,455,931
[142] U.S.P. 2,455,932

[143] U.S.P. 2,476,170
[144] B.P. 611,316
[145] B.P. 626,661
[146] U.S.P. 2,471,697
[147] Socony-Vacuum Oil Co., Ltd., U.S.P. 2,475,564
[148] Idem, U.S.P. 2,475,567
[149] B.P. 607,762
[150] U.S.P. 2,437,644
[151] U.S.P. 2,436,100
[152] U.S.P. 2,436,115
[153] B.P. 613,110
[154] B.P. 606,307
[155] B.P. 611,320
[156] U.S.P. 2,432,403
[157] B.P. 611,551. *See also* Cullinane, N.M. and Chard, S. J., *Nature*, 1948, **161**, 690
[158] U.S.P. 2,436,864
[159] U.S.P. 2,473,997
[160] B.P. 621,642
[161] Dauben, H. J., McKusick, B. C. and Mueller, G. P., *J. Amer. chem. Soc.*, 1948, **70**, 4179
[162] U.S.P. 2,475,718
[163] *J. chem. Soc.*, 1948, 1283
[164] B.P. 609,040; U.S.P. 2,451,579; Schetty, G., *Helv. chim. Acta*, 1948, **31**, 1229
[165] Swiss Pat. 240,570–2 and 236,226
[166] D.R.P. 694,662 and 698,318; FIAT Review of German Science, 'Preparative Organic Chemistry,' Pt. I, p. 269
[167] *J. chem. Soc.*, 1948, 1183
[168] U.S.P. 2,471,400
[169] FIAT Review of German Science, 'Preparative Organic Chemistry,' Pt. I, p. 270
[170] Ibid., p. 270
[171] Swiss Pat. 234,714
[172] Goll, O., FIAT Review of German Science, 'Preparative Organic Chemistry,' Pt. I, p. 271
[173] D.R.P. 706,836, ibid., p. 271
[174] D.R.P. 752,697, ibid., p. 272
[175] U.S.P. 2,458,485
[176] *J. chem. Soc.*, 1949, 1887
[177] U.S.P. 2,438,148
[178] B.P. 611,554
[179] *J. appl. Chem., U.S.S.R.*, 1947, **20**, 887
[180] U.S.P. 2,443,885
[181] BIOS Final Report No. 1484
[182] B.P. 604,491; *see also* Irving, F. and Johnson, A. W., *J. chem. Soc.*, **1948**, 2037
[183] U.S.P. 2,468,606
[184] B.P. 605,922
[185] B.P. 608,540
[186] B.P. 610,876
[187] B.P. 605,021
[188] B.P. 611,851
[189] U.S.P. 2,443,493
[190] B.P. 616,762
[191] U.S.P. 2,479,211
[192] U.S.P. 2,456,378
[193] U.S.P. 2,459,135
[194] U.S.P. 2,453,105
[195] B.P. 623,323
[196] D.R.P. 747,734; FIAT Review of German Science, 'Preparative Organic Chemistry,' Pt. I, p. 208
[197] U.S.P. 2,448,870
[198] U.S.P. 2,448,871
[199] U.S.P. 2,448,869
[200] U.S.P. 2,466,396

[201] U.S.P. 2,475,506
[202] U.S.P. 2,473,797

AZO DYES (E. L. Johnson, B.Sc., Ph.D., A.R.I.C.)

This review takes the usual form and is subdivided according to the principal uses for which the dyes are intended. There has been a decrease in the number of patents to be considered; this may be taken as an indication not so much of a diminution in research activity on the part of the manufacturers as of the fact that war-time patenting arrears have now been largely cleared. The smaller number of patents and a modest increase in available space have enabled the review to be brought up to date at October, 1949, and for this purpose a two-year period is covered for cotton dyes and azoics (omitted last year) and a one-year period for other topics.

As this year's review may be taken as indicating approximately the pattern of post-war activity in the azo dye field, it is of interest to compare the extent and direction of patenting with that obtaining ten years ago (cf. Annual Reports, 1939, **24**, 105). At that time British patents relating to azo dyes were issued at the rate of about 100 per year, whereas now the rate is less than half that figure. There are, however, to-day a number of U.S. patents emanating from U.S. firms for which there are, apparently, no British equivalents, these relating mainly to the cellulose acetate rayon and azoic fields. There has been a notable change in the direction of research activity. To-day about 35% of the patents (British and non-equivalent U.S.) relate to cotton dyes compared with only 11% in 1939; the majority of these concern after-copperable dyes which have become an item of major interest with the Swiss group of manufacturers. Wool and leather dyes are about 25% of the whole compared with 35% in 1939, azoics 15% (26% in 1939), cellulose acetate rayon dyes 20% (15%), and lakes and pigments 5% (6%). It is noteworthy that the recent big expansion in the field of new synthetic fibres has not as yet been paralleled by a corresponding increase in the number of patents for dyes of the cellulose acetate rayon class, or for dyes specifically for the new fibres, although it is known that these fibres do not always dye satisfactorily with the dyes at present available.

Messrs. Francolor and R. Lantz have described a novel method for the temporary solubilization of azoic pigments by means of *N*-sulphonic acids of secondary amino groups, the products being derived mainly from bases of the Variamine Blue type. The dyes are insolubilized by hot acid treatment and are therefore claimed to be of particular interest for application to animal fibres, being superior for this purpose to the Neocotones which require caustic alkaline development. They may also be printed on cellulosic fibres, and the similarity of the development method to that required for dyes of the Indigosol and Rapidogen classes makes them suitable for printing alongside these colours. Apart from this, there are no important advances in the art to record, the patents revealing instead steady progress along fairly well defined paths.

The mechanism of diazotization (one of the two fundamental reactions of azo chemistry), the structure of the various forms of diazo compounds

and the mechanism of their decomposition reactions are matters of sustained interest for academic research, and still provide fruitful material for chemical polemics. A few of the recent papers on these topics are mentioned below.

General

Theories of the mechanism of diazotization and nitrosation have been critically reviewed by H. H. Hodgson and W. H. H. Norris[1] who conclude that these reactions, which involve the linking of two N atoms or a N and C atom respectively, are best interpreted as a generalized aldol condensation. This is said to take place, in the case of diazotization, between undissociated nitrous acid and the free amine, the role of an acid if present being to facilitate elimination of water and to convert the *N*-nitrosamine formed initially into the corresponding diazonium salt. The photo-decomposition of *o*-hydroxydiazonium compounds has been studied by J. de Jonge and R. Dijkstra[2] who have shown that the colourless irradiation compound formed initially may be the sole product or may couple with undecomposed diazo compound, although it rapidly loses its power to couple. They have confirmed the observation of O. Süs[3] that the photo-decomposition of 1-diazo-2-naphthol gives indenecarboxylic acid, and have obtained similar results with diazonaphtholsulphonic acid.

The use of sulphamic acid for removing excess nitrous acid following the diazotization of amines is a long-established practice. H. W. Grimmel and J. F. Morgan[4] have shown that certain negatively substituted diazo compounds, such as that from 2 : 4-dinitroaniline, react quite rapidly with sulphamic acid with regeneration of the amine. With many other diazo compounds in strongly acid solution there is either no reaction (e.g. diazobenzene) or the reaction is very slow (e.g. *p*-nitrodiazobenzene). H. H. Hodgson and W. H. H. Norris[5] have shown that *p*-nitrodiazobenzene decomposes in neutral solution to give 4 : 4′-dinitrodiazoaminobenzene (40%), 4-nitro-2-4′-nitrophenylazophenol (10%), 4 : 4′-dinitrodiphenylamine (a small amount), and inseparable tar (50%).

I. V. Grachev with B. A. Porai-Koshits and other collaborators have investigated by physical means the structure of the various forms of diazo compounds and their mode of transformation with particular reference to *p*-nitrodiazobenzene.[6] Since current nomenclature is at variance with modern views on the structure of diazo compounds, they have proposed a new nomenclature which takes into account mesomeric ions and the amphoteric properties of the diazohydrate form.[7] The distribution of the three principal forms (diazonium ion, diazotate ion, and diazohydrate) at different p_H values has been calculated[8] and the reaction kinetics of the principal transformations investigated.[9] Oxidation–reduction potentials of the various forms have been determined.[10] They have also investigated the coupling of diazotized *p*-nitroaniline (*A*) with e.g. 1-*p*-sulphophenyl-3-methyl-5-pyrazolone (*E*) and have shown that coupling occurs not with the diazohydrate but with the cation of the diazo compound, optimum conditions being at the maximum concentration of the cation[11]; thus the coupling $A \rightarrow E$ occurs best at p_H 3·8–4·6 at 15° c., both higher

and lower p_H values lowering the extent of the reaction. They have also discussed[12] the diazotization reaction and favour a mechanism which is essentially that postulated by Hodgson and Norris (above).[1]

Azo compounds function as intermediates in a number of novel syntheses. H. L. Bami[13,14] has shown that diazo compounds couple with dicyanodiamide to give arylazocyanoguanidines which are hydrolysed by an acid-hydrolytic solvent mixture to arylcyanoguanidines. Azo compounds from 2 : 4-diketo-1 : 2-pyrans are shown by J. F. Morgan[15] to rearrange on heating with alkali to derivates of 4-pyridazone, e.g. 2 : 4-diketo-3-*o*-nitrophenylazo-6-methyl-1 : 2-pyran yields 4-keto-1-*o*-nitrophenyl-6-methyl-1 : 4-dihydropyridazine-3-carboxylic acid. R. H. Eastman and F. L. Detert[16] have reacted 2 : 5-dimethylfuran with *p*-nitrodiazobenzene and ethanol to give an intermediate azo compound readily converted, e.g. with aqueous alcoholic hydrochloric acid, into 3-acetyl-1-*p*-nitrophenyl-5-methylpyrazole.

The Purdue Research Foundation[17] couple diazo compounds with *sec.*-nitroalkanes so give azo compounds which may be used as dyes especially when the nitroalkane contains a tertiary amino group, e.g. 1-4′-morpholino-2-nitropropane. Coupling takes place at the C atom carrying the NO_2 group. C. I. Gochenour and E. F. Degering[18] have shown that certain nitroalcohols also react with diazo compounds to form hydrazones which, however, are not stable and decompose on keeping to give dark oils.

G. D. Parkes[19] has shown that in coupling diazo compounds with 3 : 4-dialkylphenols there is an increasing tendency to couple at the 2- rather than the 6-position as the size of the alkyl group is increased, this being attributed to steric hindrance between the *o*-alkyl groups. The coupling of pyrimidine derivatives with diazobenzene has been studied by M. Polonovski and M. Pesson[20] who have shown that those which couple always do so at the 5-position. Mono-hydroxy or -amino derivatives only couple when the substituent is in the 2-position, whereas the coupling of dihydroxy- and hydroxyamino-derivatives having one substituent in the 2-position is facilitated when the other is in the 4- or 6-position, and 4 : 6-disubstituted derivatives also couple.

B. A. Porai-Koshits and L. S. Efros[21] have carried out potentiometric titrations of azo dyes from diazotized H-acid and 1-amino-5-naphthol and its derivatives (cf. ANNUAL REPORTS, 1948, **33**, 81) and have shown that the OH is titratable only when *para* to N_2 and not when *ortho* or *peri*. When OH is *ortho* to N_2 a closed six-membered resonance ring system is formed by hydrogen bonds.

Continuing an investigation of bisulphite compounds, V. N. Ufimtsev[22] has found that chrysoidine reacts with bisulphite, not with conversion of an NH_2 group into OH as with other azo compounds, but to form a poorly soluble adduct, stable to warm dilute acids, which regenerates chrysoidine with dilute alkalis even in the cold.

V. V. Raman and M. V. Sitaraman[23] have re-examined earlier work on the preparation of azo dyes by electrolysis of solutions containing diazo component, coupling component, $NaNO_2$ and NaOH. By this means sulphanilic acid and *β*-naphthol give Orange II, but benzidine and naphthionic acid give mainly the dye naphthionic acid → naphthionic

acid and only a small amount of Congo Red, contrary to the claim of W. Löb[24] to have prepared Congo Red in this way. I. A. Pearl and A. R. Ronzio[25] have shown that the action of chlorosulphonic acid on azoxybenzene gives not the sulphonyl chloride but *p*-azobenzene chlorosulphonate which is readily hydrolysed by alkali to *p*-hydroxyazobenzene. The same reaction has been observed independently by V. O. Lukashevich and T. N. Kurdyumova[26] who have prepared a number of hydroxyazobenzenes by this route.

Azo compounds still find application for medicinal and biological purposes. Thus A. B. Wang and C-Y. Yuen[27] have prepared Prontosil analogues of the pyrazolone series by coupling e.g. diazotized sulphanilamide with 1-phenyl-3-methyl-5-pyrazolone. The preparation of 1-(4'-chloromercuriphenylazo)-2-naphthol as a coloured compound capable of attachment to biological tissue through mercapto groups only is described by H. S. Bennett and D. A. Yphantis.[28]

V. Schwarzenbach and W. Biedermann[29] have determined the acidity constants of four Eriochrome Blacks (Colour Index Nos. 201–4), e.g. Eriochrome Blue Black B—1-amino-2-naphthol-4-sulphonic acid → α-naphthol—and the formation constants of their complexes with calcium and magnesium. The dyes are shown to be very sensitive reagents for these metals.

There is some interest in polymeric and polymerizable azo compounds. R. H. Wiley and N. R. Smith[30] have investigated the reduction of *m*-nitrostyrene: zinc and hydrochloric acid gives an aminopolystyrene, zinc and caustic soda gives 3 : 3'-divinylhydrazobenzene oxidized by ferric chloride to 3 : 3'-divinylazobenzene. Zinc and ammonium chloride or sodium and methanol give 3 : 3'-divinylazoxybenzene; the two latter products can be polymerized in presence of a benzoyl peroxide catalyst. The Norsk Hydro-Elektrisk Kvaelstafaktieselskab[31] have described the preparation of macromolecular azo compounds from an aminopolystyrene (I) having a degree of polymerization greater than 1000. They are prepared by coupling diazotized (I) with a suitable coupling component, or converting (I) to hydroxypolystyrene and coupling with a suitable diazo component. The products are insoluble and have a high ion-exchange capacity; they may be used as pigments or as insoluble p_H indicators, e.g. (I) → 2-napthol-3 : 6-disulphonic acid is a brilliant red pigment. The American Cyanamid Co.[32] prepare aminoarylguanamines, e.g. 4 : 6-diamino-2-4'-aminophenyl-1 : 3 : 5-triazine, which can be used as diazo compounds for dyes capable of forming coloured resins.

In an investigation of formazyl compounds, R. Fusco and R. Romani have shown that diazo compounds react with chloromalonic acid to form *NN'*-diarylchloroformazans,[33] NAr:N·CCl:N·NHAr, which react with sodio-derivatives of β-diketones or β-ketonitriles to give the hitherto unknown 3-arylazopyrazoles.[34] Thus *NN'*-diphenylchloroformazan reacts with cyanoacetone to give 3-phenylazo-4-cyano-1-phenyl-5-methylpyrazole. R. Wizinger and V. Biro[35] have shown that arylformazans having a CO_2H or OH group *ortho* to the formazan chain are strong complex-formers, the copper and nickel complexes having an intense colour. Thus diazotized anthranilic acid reacts with benzaldehyde phenylhydrazone in strongly alkaline medium to give o-$CO_2H{\cdot}C_6H_4{\cdot}N_2{\cdot}CPh{:}N{\cdot}NHPh$

which yields a violet copper complex, the metal being bound simultaneously in two *o*-condensed rings. Complexes from compounds having one *ortho* CO_2H are decomposed by acids, but those from compounds having an *oo'*-dicarboxy configuration, e.g.

$$o\text{-}CO_2H{\cdot}C_6H_4{\cdot}N_2{\cdot}CPh{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}CO_2H\text{-}o',$$

are stable to acids.

Dyes for wool and leather

Although the number of patents to be reviewed under this heading has decreased compared with the average for the preceding two years, a greater proportion of them relate to unmetallized wool dyes as opposed to premetallized or mordant dyes. Wool dyes of this type include yellow unsulphonated monoazopyrazolones (carrying 1 to 6 halogen atoms), which have superior wet fastness to sulphonated azopyrazolones and superior levelling properties to disazo dyes, made by J. R. Geigy A.-G.[36] by coupling a 5-pyrazolone with diazotized $R'{\cdot}SO_2{\cdot}NH{\cdot}SO_2{\cdot}C_6H_4{\cdot}NH_2$ (R' = phenyl, naphthyl, *ar.*-tetrahydronaphthyl, or benzyl), light-fast combinations resulting when the NH_2 is *ortho* to SO_2 or to a halogen atom; e.g. 2-aminophenyl(1' : 2' : 3' : 4'-tetrahydro-5'- and -6'-naphthyl)disulphonimide → 1-3'-chlorophenyl-3-methyl-5-pyrazolone. Orange dyes of good fastness properties are obtained by Ciba Ltd.[37] by coupling a sulphonated diazo component, especially orthanilic acid and its derivatives, under alkaline conditions with a ureidonaphtholsulphonic acid capable of coupling *ortho* to OH, the $NH{\cdot}CO{\cdot}NH_2$ and OH groups not being *peri* to each other, e.g. orthanilic acid $\xrightarrow{\text{alk.}}$ 2-ureido-8-naphthol-6-sulphonic acid (i.e. the ureido analogue of γ acid) (yellowish-red). The same firm[38] obtain red dyes, generally very fast to light, by coupling a diazotized aminodiphenyl ether (which may be substituted but not with NO_2, sulphonic acid ester, sulphonamide, or CF_3), especially those having NH_2 *ortho* to the ether link, under acid conditions with a 2-naphthylaminesulphonic acid having a free 1-position, and which may contain nuclear substituents, especially OH, e.g. 4 : 2'-dichloro-2-aminodiphenyl ether $\xrightarrow{\text{acid}}$ γ acid (bluish-red).

Dyes giving yellow to red shades are obtained by the Eastman Kodak Co.[39] by coupling a tetrazotized diamine

$$NH_2{\cdot}R{\cdot}X{\cdot}NMe{\cdot}C_6H_4{\cdot}NMe{\cdot}X'{\cdot}R'{\cdot}NH_2$$

(R and R' are benzenoid or naphthalenoid radicals, and X and X' are CO, SO_2, or $O{\cdot}CH_2{\cdot}CO$) with suitable coupling components. According to constitution the products are suitable for dyeing cellulose esters or wool, e.g. *NN'*-bis-*p*-aminobenzoyl-*NN'*-dimethyl-*p*-phenylenediamine $\rightrightarrows$ (1-naphthol-4-sulphonic acid)$_2$, which dyes wool scarlet. Ciba Ltd. have two patents relating to blue dyes from 1-arylaminonaphthalene-8-sulphonic acids (aryl-*peri* acids) as end component. Thus they couple a diazotized amine, which may contain azo groups, with an aryl-*peri* acid in which the aryl group is the residue of a diaryl ether, e.g. H-acid → *p*-phenoxyphenylperi acid (E), and metanilic acid → α-naphthylamine → E, the latter being an analogue of the well known Sulphon Cyanine type of dye which has phenyl- or *p*-tolyl-peri acid as end component.[40] They also

make dyes of the Sulphon Cyanine type having superior washing fastness in which the first component is an amine of the type :

$$SO_3H{\cdot}C_6H_4{\cdot}N(Alkyl){\cdot}SO_2{\cdot}C_6H_4{\cdot}NH_2,$$

especially those having NH_2 *meta* to SO_2.[41] An example is $SO_3H{\cdot}C_6H_4{\cdot}NMe{\cdot}SO_2{\cdot}C_6H_4{\cdot}NH_2$-*m* → α-naphthylamine → phenyl-*peri* acid (navy-blue).

Among patents for metallizable wool dyes there are several relating to dyes specifically for use in the one-bath chroming process. Yellow dyes of this type are obtained by Imperial Chemical Industries Ltd.[42] by coupling diazotized 5-sulphoanthranilic acid with 1–4′-(2″-or 4″-chlorophenoxy)phenyl-3-methyl-5-pyrazolone, the products giving bright yellow shades of excellent fastness to wet treatments and light. Fast bluish-green dyes are obtained by the same firm[43] by coupling diazotized 4-nitro-2-aminophenol-6-sulphonic acid (*A*) with a 1-amino-8-naphthol-3 : 6-di(sulphonyl-mono- or -di-alkylamide), the alkyl groups on each N atom totalling 2-4C, e.g. A → 1-amino-8-naphthol-3 : 6-di(sulphonyl-dimethylamide). Blue to bluish-green dyes obtained by J. R. Geigy A.-G.[44] are of the pattern : 4-chloro- (bluish-grey) and 3 : 4-dichloro-5-nitro-2-aminophenol-6-sulphonic acid → 5 : 8-dichloro-1-naphthol (greenish-blue). Bright green shades are obtained by the one-bath chrome process from the dye 4-nitro-2-aminophenol-6-sulphonic acid → 1-phthaloyl-amino-7-naphthol prepared by the General Aniline & Film Corporation.[45]

There are no patents for review relating solely to pre-chromed dyes. Dyes which may be metallized in substance or on the fibre and giving violet to green or grey shades are obtained by J. R. Geigy A.-G.[46] by coupling a diazotized amine having a lake-forming group in the *ortho* position and which may contain an azo group with a 1-naphthol-8-sulphonic acid having a methyl or benzyl group in the 4-position, e.g. 4-chloroaniline-3-sulphonic acid → 3-amino-*p*-cresol → 4-methyl-1-naphthol-8-sulphonic acid, which dyes wool violet, after-chromed to green.

The American Cyanamid Co. have continued their investigations of chromable dyes from 4-diazo-5-pyrazolones (cf. ANNUAL REPORTS, 1948, **33**, 86). Thus they couple a 4-diazo-1-sulphophenyl-3-methyl-5-pyrazolone with a component containing an enolizable keto group, and metallize in substance or on the fibre, e.g. the chromium complex of 4-amino-1-4′-sulphophenyl-3-methyl-5-pyrazolone → 1-4′sulphophenyl-3-methyl-5-pyrazolone which gives mustard-yellow dyeings.[47] They also prepare dyes of the pattern : 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone (4-aminoantipyrine, *A*) → component coupling *ortho* to OH or NH_2, for conversion to chromium complexes, e.g. *A* → 2-naphthol-6-sulphonic acid, yellowish-red on wool when after-chromed.[48] It is suggested that the ready formation of chromium complexes in the latter case is due to the pyrazolone system's (which formally cannot enolize) reacting as a betaine.

Disazo dyes giving green to olive shades on wool or nylon, the fastness of which may be improved by after-chroming, made by the Allied Chemical & Dye Corporation,[49] are of the pattern : an *o*-aminophenol or an anthranilic acid $\xrightarrow{\text{alk.}}$ 1-amino-8-naphthol-4-sulphonic acid (S-acid) → an aceto-acetanilide, e.g. 4-nitro-2-aminophenol → S-acid → acetoacet-*o*-anisidide.

A dye giving grey to black shades on leather obtained by Imperial Chemical Industries Ltd.[50] has the constitution : aniline-2 : 5-disulphonic acid $\xrightarrow{\text{alk.}}$ H-acid $\xleftarrow{\text{acid}}$ benzidine $\rightarrow$ *m*-aminophenol $\leftarrow$ aniline-2 : 5-disulphonic acid. Owing to its low toxicity it is also valuable for colouring foodstuffs.

Dyes for cotton

Research on direct cotton dyes in recent years has been directed in the main towards obtaining products of higher fastness, particularly to light and wet treatments such as laundering, vat-dye fastness combined with ease of application being the obvious objective. It cannot be said that this objective has yet been achieved, and it may prove to be unattainable with the conventional type of direct cotton dye, but patent specifications indicate that an increasingly high standard is being aimed at by manufacturers.

Increased light fastness in azo compounds is frequently sought by conversion to metal complexes either in substance or on the fibre during or after dyeing, the metal most favoured for cotton dyes being copper. With regard to wet fastness, it is obvious that water-soluble compounds applied as such to cellulose will inevitably show some looseness to washing unless they undergo a treatment after dyeing which renders them less soluble. Several such after-treatments are, of course, available, e.g. the well known method of diazotizing a suitably constituted dye and coupling with a developer such as β-naphthol, and after-treatment with formaldehyde. After-treatment with metal salts, too, often produces decreased solubility, although the metal complexes formed are not always stable to subsequent alkaline (e.g. soap) treatment, but with suitably chosen dye constitutions a notable improvement in wet fastness can be achieved. Thus, the fact that after-metallization can be used to improve both light and wet fastness explains why dyes designed for this purpose have received such abundant attention recently, particularly from the Swiss group of manufacturers, and the bulk of the patents reviewed here come within this class.

Apart from fastness requirements of the ultimate consumer, the introduction of new finishing processes which the dyed material has to undergo present the dye manufacturer with new problems. Thus the increasing importance of the anti-crease process for viscose rayon has created a demand for dyes which will withstand the process without loss of light fastness, particularly blue dyes since many of the light-fast direct blues are adversely affected in this respect.

In patents relating to metallizable dyes, provision is very frequently made for metallization to take place either in substance, or on the fibre during or after dyeing, although in the majority of cases the main emphasis is on one or other of these procedures.

Considerable attention has been devoted recently to pre-formed copper complexes derived from the original azo direct-cotton blues which were disazo dyes of the pattern : $E^1 \leftarrow$ dianisidine $\rightarrow E^2$, E^1 and E^2 being naphthol- or aminonaphthol-sulphonic acids, and were first marketed in the closing years of the last century, e.g. Benzoazurine G (Colour Index No. 502, $E^1 = E^2 =$ 1-naphthol-4-sulphonic acid). These original dyes

can be after-coppered on the fibre to give an improvement in light fastness, which, however, is often not permanent and is destroyed by alkaline (e.g. soap) treatments. A better method which converts the dyes in substance into copper complexes which are stable to alkalis is well known, the essential feature being that the alkyl groups of dianisidine are split off giving a copper complex in which two hydroxy groups *ortho* to each azo group are involved.[51] In a number of cases the manufacturers claim that the copper-complex dyes are unimpaired in light-fastness by the anti-crease process.

Thus with dyes of the pattern: copper complex of $E^1 \leftarrow$ dianisidine $\rightarrow E^2$, E. I. Du Pont de Nemours & Co.[52] obtain violet to blue shades of excellent light-fastness unimpaired by anti-crease treatment when $E^1 = E^2 =$ 2-naphthol-6-sulphonic acid, or 1-naphthol-3- or -5-sulphonic acid. The Clayton Aniline Co.[53] have E^1 and E^2 the same or different naphthol-mono- or -di-sulphonic acids (devoid of NH_2, CO_2H, and alkoxy), but excluding 2-naphthol-6-sulphonic acid in dyes containing only two SO_3H, e.g. the dye giving a bright reddish-blue on cotton when $E^1 = E^2 =$ 2-naphthol-3 : 6-disulphonic acid. Sandoz Ltd.[54] have $E^1 =$ 1-naphthol-3 : 6 : 8-trisulphonic acid and $E^2 =$ J-acid or an *N*-substituted derivative which may carry an azo group in the 1-position to obtain blue dyes of excellent exhaustion and very good fastness to light and washing. Ciba Ltd.[55] obtain blue dyes having pronounced fastness to light, in some cases unaffected by anti-crease treatment, when $E^1 =$ a dihydroxynaphthalenemonosulphonic acid and E^2 a naphtholsulphonic acid, e.g. reddish-blue when $E^1 =$ 2 : 8-dihydroxynaphthalene-6-sulphonic acid and $E^2 =$ 2-naphthol-6-sulphonic acid.

Similar dyes are obtained by the Clayton Aniline Co.[56] by coupling tetrazotized dianisidine with 1 mol. of an acylaminonaphthol-mono- or -di-sulphonic acid (excluding acyl derivatives of 2S-acid, i.e. 1-amino-8-naphthol-2 : 4-disulphonic acid) and 1 mol. of either (*a*) the same or a different acylaminonaphthol sulphonic acid, (*b*) a component containing an OH or $CO{\cdot}CH_2$ group (but devoid of NH_2) and capable of coupling *ortho* to OH, or (*c*) 2S-acid, converting to the copper complex with ammoniacal copper sulphate or (in a patent of addition)[57] other aqueous solutions containing cuprammonium ions, or with cupritetrammine compounds derived from organic bases, and then hydrolysing the acyl groups (without destroying the copper complex) with dilute acid or alkali. It is claimed that this procedure avoids decomposition which is experienced when the free amino compounds are coppered. For example, dianisidine $\rightrightarrows$ (acetyl-H-acid)$_2$ is converted to its copper complex and the acetyl groups hydrolysed with hot 3–4% sodium hydroxide solution to give a dye yielding bright greenish-blue shades of good light-fastness.

A further step in the exploitation of dyes of the dianisidine type has been the use by Ciba Ltd. of 3 : 3′-dihydroxybenzidine (D^1) instead of dianisidine as tetrazo component to give dyes which can be converted on the fibre by a simple after-coppering process to metal complexes which could not be obtained from the corresponding dyes from dianisidine except under reaction conditions applicable only in substance and not on the fibre (cf. ANNUAL REPORTS, 1946, **31**, 109). A useful exposition of the various developments in the use of copper in conjunction with azo

direct dyes has been given by E. Krähenbühl[58] of the Ciba Co., the use of D^1 in making dyes related to their 'Coprantine' series of after-copperable dyes being described.

In order to bring about complete coupling of each of the two diazo groups of tetrazotized D^1 it is desirable, and in some cases essential, to use a medium of high p_H such as that produced by alkali or alkaline-earth hydroxides (this coupling method being claimed)[59] and the products so obtained differ from those described earlier from the same diamine when alkali carbonate was apparently used as coupling medium.[60] In a closely related series of patents,[61] dyes are obtained for after-coppering on the fibre when tetrazotized D^1 is coupled (i)[62] with 2 mols. of the same or different coupling components at least one being a dihydroxynaphthalene devoid of SO_3H, e.g. $D^1 \rightrightarrows$ (2 : 6-dihydroxynaphthalene)$_2$ (navy-blue); (ii)[63] with 2 mols. of coupling components at least one having a secondary or tertiary N atom, and any naphthalenoid component being sulphonated, e.g. $D^1 \rightrightarrows$ (1-phenyl-3-methyl-5-pyrazolone)$_2$ (ruby-red), and $D^1 \rightrightarrows$ (di-J-acid)$_2$ (blue); (iii)[64] with 2 mols. of coupling components at least one being a 1-naphtholsulphonic acid with an auxochrome group in the 8-position, e.g. $D^1 \rightrightarrows$ (1-amino-8-naphthol-4-sulphonic acid)$_2$ (blue); and (iv)[65] with 2 mols. of a naphthol (preferably *ortho* coupling) devoid of SO_3H and containing one other substituent (especially an auxochrome) except OH or NH_2 *peri* to OH, e.g. $D^1 \rightrightarrows$ (1-amino-7-naphthol)$_2$ (grey). An interesting feature of a number of the dyes exemplified is that they are devoid of water-solubilizing groups such as SO_3H and CO_2H. Dyeing takes place from baths containing alkali hydroxide or carbonate, in which the dyes are soluble, and after-coppering can proceed in the same bath by using, for example, a complex copper tartrate.[66]

The value of the urea grouping in azo cotton dyes has been known for many years; for example, Cotton Yellow G, 4 : 4′-diaminodiphenylurea $\rightrightarrows$ (salicylic acid)$_2$ (Colour Index No. 346), has been on the market since 1888, and this constitutional factor still features widely in patent specifications. J. R. Geigy A.-G.[67] couple a tetrazotized 2 : 5 : 2′ : 5′-tetra-alkoxy-4 : 4′-diaminodiphenylurea (D^2) either with 2 mols. of 2S-acid or with 1 mol. each of 2S-acid and another hydroxy-compound coupling *ortho* to OH which may carry azo groups, subsequently converting to the copper complex in substance or on the fibre, e.g. 2S-acid $\leftarrow$ D^2(alkoxy = OMe) $\rightarrow$ 2-naphthol-6-sulphonic acid which dyes blue and can be after-coppered to improve wet and light fastness. Ciba Ltd.[68] couple tetrazotized 4 : 4′-diaminodiphenylurea-3 : 3′-dicarboxylic acid (D^3) with 2 mols. (the same or different) of an arylpyrazolone containing sulphonamide groups to give metallizable dyes primarily for after-coppering and giving yellow to brown shades of high light-fastness, e.g. $D^3 \rightrightarrows$ (1-3′-sulphamylphenyl-3-methyl-5-pyrazolone)$_2$ (brownish-yellow). They also[69] prepare dyes giving yellow to brown shades of high light fastness when after-coppered of the pattern: (substantive diamine with SO_3H or $SO_2 \cdot NH_2$ *ortho* to each NH_2 and containing a urea or 1 : 3 : 5-triazine grouping, but devoid of azo or azoxy groups) $\rightrightarrows$ 2 mols. (the same or different) of a 3-methyl-5-pyrazolone with a salicylic acid radical in the 1-position attached either directly or through a bridge member, any of the possible alternative preparative methods being employed as convenient. For

example, the nitro group of the monoazo compound: 4-nitroaniline-2-sulphonic acid $\rightarrow$ 1-(4′-hydroxy-3′-carboxyphenyl)-3-methyl-5-pyrazolone is reduced, the resulting amino compound condensed with *p*-nitrobenzoyl chloride, the nitro group reduced, and the aminobenzoyl compound treated with phosgene to double the molecule (yellow). J. R. Geigy A.-G. have two patents concerning (*a*) monoazo and (*b*) polyazo copperable dyes related to Benzo Fast Copper Red RL (I.G.)[70] from ureas or thioureas of 1-(aminoaryl)-5-pyrazolones. Monoazo dyes[71] giving orange to red shades are obtained by coupling 1 mol. of 6-nitro-1-diazo-2-naphthol-4-sulphonic acid (*A*) with the urea or thiourea of a 1-4′-aminophenyl-(or 1-4″-aminodiphenylyl)-5-pyrazolone having methyl, ethyl, or phenyl in the 3-position, e.g. $A \rightarrow$ the urea (B) of 1-4′-aminophenyl-3-methyl-5-pyrazolone (brownish-orange, redder when after-coppered). The polyazo dyes[72] giving orange to violet shades are of the pattern: $A \rightarrow Z \leftarrow D^4 \rightarrow E$ where Z is the urea or thiourea of a 1-4′-amino-phenyl-5-pyrazolone having alkyl, phenyl, CO_2H, or a CO_2H derivative in the 3-position, D^4 is a diamine, E is any coupling component which may also contain azo groups, and A is as above, several alternative preparative methods being available. An example is 4 : 4′-diaminodiphenylurea $\rightrightarrows (B \leftarrow A)_2$ (brownish-red, after-coppered to red). Ciba Ltd.[73] prepare dyes after-copperable on cellulose to give red shades of good fastness to light and washing by phosgenating, either alone or in admixture with other aminoazo compounds, the aminodisazo compounds $R'{\cdot}N_2{\cdot}R''{\cdot}N_2{\cdot}R'''{\cdot}NH_2$, where R', R'', and R''' are benzene nuclei, R' contains an *o*-hydroxycarboxy grouping, R'' an SO_3H group, and the NH_2 and azo groups of R''' are *para* to each other, e.g. 5-(4′-amino-2′-sulphophenylazo)salicylic acid $\rightarrow$ cresidine, phosgenated (red). Sandoz Ltd.[74] phosgenate a 5-(4′-aminophenylazo)-3-sulphosalicylic acid which may have alkyl or alkoxy in the 5′- and alkyl, alkoxy or acylamino in the 2′-positions. The resulting dyes give yellow shades which become outstandingly fast to light and washing by treatment with a copper-yielding substance in presence of a water-soluble high-molecular poly-amino compound of the type used in improving the wet fastness of dyeings, the improvement in light fastness, contrary to experience with many other dyes, being greater than that obtained with copper compounds alone.

For brown shades, the general pattern of the old Congo Brown G, salicylic acid $\leftarrow$ benzidine $\rightarrow$ resorcinol $\leftarrow$ sulphanilic acid (Colour Index No. 598), is still being used, although provision of additional metallizable points in the molecule is now usual. The General Aniline & Film Corporation[75] claim dyes of the pattern: a salicylic acid $\leftarrow$ a 4 : 4′-diaminodiphenyl $\rightarrow$ resorcinol or a derivative $\leftarrow$ an aminosalicylic acid (including sulphonated derivatives), this patent covering the manufacture in the United States of Benzo Fast Copper Brown BRL (I.G.).[76] Similar after-copperable brown dyes obtained by Sandoz Ltd.[77] are of the pattern: a salicyclic acid $\leftarrow$ a diaminobenzanilide $\rightarrow$ resorcinol $\leftarrow$ an aminoazo compound having OH *ortho* to NH_2, e.g. salicylic acid $\leftarrow$ 4 : 4′-diamino-benzanilide $\rightarrow$ resorcinol $\leftarrow$ (naphthionic acid $\rightarrow$ *N*-acetyl-*o*-aminophenol, hydrolysed). Yellowish to reddish-brown shades, substantially unaltered in shade but greatly improved in wet- and light-fastness by after-coppering, are obtained by J. R. Geigy A.-G.[78] from dyes of the pattern:

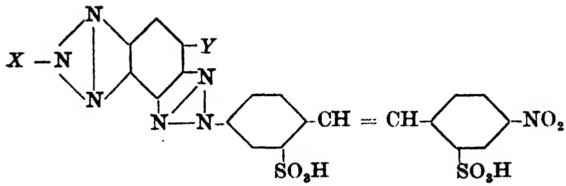
a 3-methyl-5-pyrazolone (having H, alkyl, or aryl in the 1-position) ← a diamino-diphenyl, -diphenylurea, or -benzanilide → resorcinol ← amine having OH or group convertible to OH under metallization conditions in the *o*-position, at least one SO_3H being present, e.g. 1-phenyl-3-methyl-5-pyrazolone ← benzidine → resorcinol ← 6-chloro-2-aminophenol-4-sulphonic acid (brown, after-coppered).

J. R. Geigy A.-G.[79] also prepare brown dyes primarily for after-coppering of the pattern: component coupling *ortho* to OH or NH_2 ← a 1 : 3-diaminobenzene-5-sulphonic (or -carboxylic) acid having OH or group convertible into OH (i.e. Cl, OCH_3) in the 2-position (D) → resorcinol ← $NH_2 \cdot R \cdot N_2 \cdot C_6H_3(OH) \cdot CO_2H$, R being a mono- or multi-nuclear benzenoid radical or a naphthalenoid radical, and the OH and CO_2H groups being *ortho* to each other; e.g. 1-naphthol-4-sulphonic acid ← 2 : 6-diamino-phenol-4-sulphonic acid → resorcinol ← benzidine → salicylic acid (reddish-brown). The diamine (D) may be tetrazotized as such and coupled stepwise, or its mono-N-acetyl derivative may be diazotized and coupled, the acetyl group hydrolysed, and the resulting aminoazo compound diazotized and coupled, an unusual modification of the latter procedure being hydrolysis of the acetylaminodiazo compound at 40–45° before coupling. It is claimed that both the azo groups derived from the diamine (D) participate in metal complex formation on after-coppering.

For yellow to brown shades of good light fastness, dyes containing stilbene residues continue to be investigated, and the complexity of the molecule is often increased by linking together two or more aminoazo residues by means of a 1 : 3 : 5-triazine radical, as well as provision being made for metallization. Azo stilbene dyes containing a 1 : 3 : 5-triazine nucleus and primarily intended for after-coppering on the fibre to give yellow to brown shades are made by Ciba Ltd.,[80] e.g. by condensing 1 mol. of 4 : 4′-diaminostilbene-2 : 2′-disulphonic acid with 2 mols. of cyanuric chloride and reacting the product (I) (containing 4 replaceable halogen atoms) with 3 mols. of p-$X \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH) \cdot CO_2H$ (where X is NH_2 or *m*- or p-$NH_2 \cdot C_6H_4 \cdot CO \cdot NH$, and the OH and CO_2H groups are *ortho* to each other) and 1 mol. of any aminoazo compound. The same products can also be obtained by obvious alternative routes. An example is (I) condensed with 4 mols. of 5-(4′-aminophenylazo)salicylic acid, the product dyeing a greenish-yellow becoming redder and stronger on after-coppering. Similar dyes are obtained by J. R. Geigy A.-G.[81] by condensing 1 mol. of 4 : 4′-diamino-stilbene (or -dibenzyl) or a 2 : 2′-disulpho or 2 : 2′-dicarboxy derivative with 2 mols. of a cyanuric halide, and reacting the product with at least 1 mol. of an aminoazo compound or an amine from which azo compounds can be derived, any remaining halogens of the primary condensation product being reacted with ammonia or other amines. Dyes of this type described earlier, including those of the preceding case, are excluded from the claims. According to the constitution of the azo part of the molecule, dyes, generally yellow to brown in shade, can be obtained which are suitable for diazotization and coupling, for coupling with diazotized amines, for metallization, or for after-treatment with formaldehyde, the last being of particular interest. An example is (I) condensed with 2 mols. of 3-(4′-aminophenylazo)benzene sulphonic acid and then with an excess of dimethylamine to give a yellow

dye of good light fastness improved in wet fastness by after-treatment with formaldehyde.

J. R. Geigy A.-G.[82] obtain stilbene dyes by condensing in alkaline solution isocyclic or heterocyclic amines (including aminoazo compounds) of their saponifiable acyl derivatives with a nitrostilbene-bis-triazole (II) of probable general formula :



(X is a phenyl or naphthyl radical containing at least one solubilizing group, and Y is H, alkyl, alkoxy, SO_3H, CO_2H, or halogen). The stilbene-triazoles (II) are obtained by oxidizing (e.g. with copper sulphate in alkaline solution) *o*-aminoazo compounds obtained by coupling diazotized 4′-nitro-4-aminostilbene-2 : 2′-disulphonic acid (A) with a 5-amino-2-aryl-2 : 1 : 3-benztriazole. For example, A → 5-amino-2-(4′-hydroxy-3′-carboxyphenyl)-2 : 1 : 3-benztriazole is oxidized to the bis-triazole and condensed with 5-(4′-aminophenylazo)salicylic acid, the product dyeing cotton yellow, wet fastness being improved by after-chroming. A condensation reaction similar to that of nitrostilbenes and probably resulting in the formation of azoxy groups takes place when a 5-(4′-nitrophenylazo)salicylic acid is condensed in alkaline solution with an aminodiphenylamine containing at least one solubilizing group. The products, described by J. R. Geigy A.-G.,[83] are suitable for the dyeing of wool and leather, and for the chrome-printing of cotton, e.g. the condensation product of 5-(4′-nitro-2′-sulphophenylazo)salicylic acid and 4-aminodiphenylamine-2-sulphonic acid gives a reddish-brown by chrome-printing.

Other metallizable dyes containing the triazine nucleus, and giving red-brown shades, are obtained by Ciba Ltd.[84] by coupling a diazotized unsulphonated *o*-aminophenol with the ternary condensation product of 1 mol. of cyanuric chloride with 1 mol. of J-acid and either (a) 1 mol. each of an unsulphonated 5-(4′-aminophenylazo)salicylic acid (III) and a benzenoid arylamine, or (b) 2 mols. of (III). The dyes may also be obtained by alternative routes. An example is: 2-aminophenol-4-sulphonamide → ternary condensation product of cyanuric chloride with 1 mol. each of J-acid, (III), and aniline. Dyes described as having similar properties are the mixed ureas obtained by phosgenating an *o*-aminophenol $\xrightarrow{\text{alk.}}$ J-acid with (III) or the same products obtained by other routes. After-copperable grey dyes obtained by the same firm[85] are of the pattern: aminosalicylic acid → M^1 → M^2 → binary or ternary condensation product of cyanuric chloride with 1 mol. of J-acid and 1 or 2 mols. (the same or different) of an arylamine incapable of dye formation by diazotization and coupling and devoid of an *o*-hydroxycarboxy grouping, M^1 and M^2 being naphthalenoid middle components, e.g. 5-aminosalicylic acid → 1 : 7-Cleve's acid → α-naphthylamine → ternary

condensation product of cyanuric chloride with 1 mol. each of J-acid, metanilic acid, and aniline.

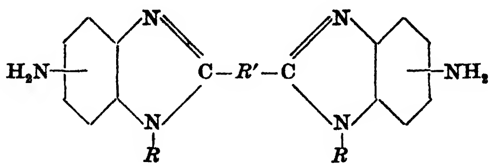
Among miscellaneous metallizable dyes obtained by Ciba Ltd. are [5-(4′-amino-3′-carboxyphenylazo)salicylic acid]$_2$ $\rightrightarrows$ di-J-acid which gives greenish-blue shades of superior washing fastness when after-coppered,[86] and the products obtained by coupling a diazotized 2-aminophenol containing CO·NH*R* (*R* = alkyl, aralkyl, aryl or heterocyclic radical) in the 4- or 6-position with J-acid or a *N*-substituted derivative. The latter, which are copperable in substance or on the fibre, give red to brown shades, an example being [2 : 1 : 4-$NH_2 \cdot C_6H_3(OH) \cdot CO \cdot NHPh]_2$ $\rightrightarrows$ the ternary condensation product of cyanuric chloride with 2 mols. of J-acid and 1 mol. of aniline (ruby-red when after-coppered).[87]

Grey dyes, primarily intended for after-coppering, are prepared by J. R. Geigy A.-G.[88] by coupling 2 mols. (the same or different) of a diazotized nitro- (or acylamino-)aniline (at least 1 mol. containing a lake-forming group) with 1 mol. of a 1-amino-8-naphthol-3- or -4-sulphonic acid or -3 : 6- or -4 : 6-disulphonic acid (the couplings being made successively first under acid and then under alkaline conditions), converting the nitro or acylamino groups to amino by reduction or hydrolysis, and tetrazotizing the product and coupling with 2 mols. of a naphthol end-component which may contain azo groups, *e.g.* (*p*-nitroaniline $\xrightarrow{\text{acid}}$ H-acid $\xleftarrow{\text{alk.}}$ 6-nitro-anthranilic acid), reduced $\rightrightarrows$ (5-aminosalicylic acid $\xrightarrow{\text{acid}}$ J-acid)$_2$. The use by the same firm of an aminodiaryl ketone containing an *o*-hydroxycarboxy grouping in the aryl nucleus not carrying the NH_2 as a diazo component was mentioned last year in the review of wool-dye patents.[89] Dyes from amines of this type suitable for vegetable fibres are exemplified by: (3-amino-4 : 4′-dihydroxy-3′-carboxybenzophenone)$_2$ $\rightrightarrows$ carbonyl-J-acid which gives a ruby-red when after-coppered on cotton, but may be coppered in substance and then after-chromed on the fibre to improve wet fastness.

Difficulty often experienced in obtaining good white discharges of material dyed with coppered azo dyes (including those after-coppered) has tended to nullify the advantage of ready dischargeability which most azo dyes possess in the absence of copper. A method claimed to give improved whites described by Ciba Ltd.[90] consists in treating material which has been discharged by the usual sulphoxylate method with an aqueous solution of ammonia or a basic amine such as ethanolamine. J. R. Geigy A.-G.[91] treat the material before, during, or after the discharging operation with a component yielding cyanide ions, including metal cyanides and cyanohydrins such as that from benzaldehyde-*m*-sulphonic acid.

There are one or two cases of dyes specificially intended for after-treatments other than metallization. Dyes for diazotization and development on the fibre made by Sandoz Ltd.[92] are of the pattern: a 5-*p*′-aminobenzoylaminosalicylic acid → a 3-alkyl-, -alkoxy-, or -acylamino-aniline (optionally with alkyl or alkoxy in the 6-position) → *p*-amino-benzoyl-J-acid (*E*), and give red to blue shades which are improved in wet fastness by diazotization and development with β-naphthol. The products are suitable for dyeing viscose which is to be anti-creased. An

example is: 5-p'-aminobenzoylaminosalicylic acid → m-toluidine → E (red-bordeaux, slightly bluer on development). Ciba Ltd.[93] couple a tetrazotized diaminodibenziminazole (IV) of general formula—



(R = H, alkyl; R' = a bivalent hydrocarbon radical of at least 2C) with a pyrazolone to obtain yellow to red dyes. The pyrazolone is preferably an arylpyrazolone containing a diazotizable amino group so that the dyes may be diazotized and developed. An example is (IV) (R = H, R' = $\text{-CH}_2\cdot\text{CH}_2\text{-}$) $\rightrightarrows$ (1-3'-aminophenyl-5-pyrazolone-3-carboxylic acid)$_2$ which dyes cotton orange, diazotized and developed with β-naphthol to a bright yellowish-red, fast to washing and light.

Continuing their investigations of dyes of the type intended for after-treatment with formaldehyde to give improved wet fastness, E. I. Du Pont de Nemours & Co.[94] make green tetrakisazo dyes of the pattern: resorcinol ← D → 2-alkoxy-1-naphthylamine-6 (or 7)-sulphonic acid → an amino-benzoyl-J-acid → a 1-aryl-5-pyrazolone. The component D is a 1 : 4-naphthylene- or 1 : 4- or 1 : 3-phenylenediamine which is diazotized and coupled initially as a mono-N-acyl derivative, the acyl group being eventually hydrolysed before diazotization and coupling to resorcinol. Both the direct and formaldehyde-treated dyeings may be after-coppered. An example giving bright green shades of excellent fastness to washing and readily dischargeable is: [p-aminoformanilide → 2-methoxy-1-naphthylamine-6-sulphonic acid → m-aminobenzoyl-J-acid → 1-(2' : 5'-dichloro - 4' - sulphophenyl) - 3 - methyl - 5 - pyrazolone] hydrolysed, → resorcinol.

Patents for dyes which are not pre-metallized and which are not intended for after-metallization or other after-treatment are nowadays comparatively infrequent. The General Aniline & Film Corporation[95] obtain bright bluish-red disazo dyes by the phosgenation of a p-amino-benzoyl or p'-aminobenzoyl-p-aminobenzoyl derivative of the monoazo dye (p-nitroaniline → 2-amino-8-naphthol-3 : 6-disulphonic acid) reduced (V), which are said to be considerably brighter than the phosgenation product of (V) itself. Linear trisazo dyes giving grey shades fast to light and boiling made by Ciba Ltd.[96] are of the pattern: 4-nitro-aniline or -1-naphthylamine → M^1 → M^2 → an aminonaphtholsulphonic acid substituted on the amino group with a 2-1 : 3 : 5-triazine radical, the groups at positions 4 and 6 of the triazine nucleus being incapable of azo-compound formation either by diazotization or coupling (M^1 and M^2 are naphthalenoid middle components); e.g. p-nitroaniline → 1 : 7-Cleve's acid → 1 : 7-Cleve's acid → condensation product of cyanuric chloride with 1 mol. each of J-acid, metanilic acid, and aniline.

Azoics

Novel diazo components prepared by the American Cyanamid Co. for use as bases in the azoic process are (i)[97] benzenoid amines containing at least one SO_2F group, e.g. *o*-toluidine-4-sulphonyl fluoride (*A*) which gives greenish-yellow shades with bisacetoacet-*o*-tolidide; (ii)[98] the aminoazo compounds $R{\cdot}N_2{\cdot}R'{\cdot}NH_2$, where R is a benzenoid radical and R' a benzenoid or naphthalenoid radical, at least one containing the SO_2F group (which lightens and brightens the shade), e.g. $A \rightarrow \alpha$-naphthylamine which gives bluish-grey with 2-hydroxy-3-naphthanilide; (iii)[99] the aminodiphenylamine derivatives obtained by condensing an amino-1 : 4-benzdioxan with a *p*-nitrohalogenobenzene and reducing the nitro group which give violet to blue shades, e.g. 6-*p*-aminophenylamino-1 : 4-benzdioxan; and (iv)[100] halogenoalkyl ethers of 4-amino-4′-hydroxydiphenylamine, e.g. the 2-chloroethyl ether giving blue with 2-hydroxy-3-naphthanilide. Green azoic shades or pigments are obtained by Imperial Chemical Industries Ltd.[101] from an aminophthalocyanine containing at least two amino groups in aryl nuclei and a 'yellow-forming' coupling component, e.g. brilliant yellowish-green azoic shades from copper tetra-4-(*p*-aminobenzoyl)phthalocyanine and bisacetoacet-*o*-tolidide.

Novel coupling components prepared by the American Cyanamid Co.[102] for use in the the azoic process and in the preparation of pigments are the arylamides from 2-hydroxy-3-naphthoic acid and 6-amino-1 : 3- or -1 : 4-benzdioxan. The same firm[103] use 2-hydroxy-3-naphthoic-4′-chloro-2′-ethylanilide for azoic combinations of high light fastness and for pigments of good bleed resistance, both these properties being inferior if Et is replaced by Me.

Coupling components for yellow shades prepared by Société Anonyme de Matières Colorantes et Produits Chimiques Francolor[104] (hereafter called Francolor) are acylacetyl derivatives of an aminobenzthiazole, the amino group being in the benzo nucleus, e.g. the terephthaloylacetyl derivative of 6-amino-2 : 5-dimethoxybenzthiazole which gives bright yellow with 2 : 5-dichloroaniline. The General Aniline & Film Corporation[105] condense *o*-hydroxycarboxylic acids with an *o*-, *m*-, or *p*-4-morpholinoaniline to give products of low cotton substantivity specially suitable for printing, e.g. 2-hydroxy-3-naphthoic-4′-4″-morpholinoanilide which gives orange shades with 2-chloro-5-trifluoromethylaniline.

Francolor[106] use a 7-aminoindazole devoid of water-solubilizing groups for preparing azoic combinations which have the property of forming copper complexes, the coppering being effected either during coupling or subsequently; e.g. cotton impregnated with 2-hydroxy-3-naphthoic-β-naphthylamide is treated in a bath containing diazotized 7-aminoindazole and copper acetate to given a corinth shade fast to light and boiling. Metallic complexes of insoluble indazole dyes have also been studied by P. Petitcolas and R. Sureau.[107] The same firm prepare[108] temporarily solubilized azoic pigments from *NN′*-disulphonic acids of arylenediamines having one primary and one secondary amino group, especially those related to Variamine Blue B. Nitrous acid effects diazotization and elimination of SO_3H on the primary N, and coupling with an azoic component gives a product which is water-soluble by virtue of the SO_3H

on the secondary N. The products, which are stable under alkaline or neutral conditions, may be used[109] for dyeing, e.g. wool, the dyed material being subsequently treated with hot dilute acid which eliminates the remaining SO_3H, the dyeing undergoing a bathochromic shade-change in the process; e.g. 4-amino-4′-methoxydiphenylamine-N^1-sulphonic acid → 2-hydroxy-3-naphthoic-*p*-anisidide which dyes wool violet-red from an ammonium acetate bath becoming blue, fast to light and wet treatments, on development in a boiling dilute sulphuric acid bath. The products may also be used for printing cellulose. The preparation and diazotization of the amines involved and the application of the resulting dyes have also been described by R. Lantz.[110,111]

Dyes for cellulose acetate rayon

Dyes designed for cellulose acetate rayon are usually applicable also to the newer synthetic fibres such as nylon, and vinyl polymers and copolymers, e.g. Vinyon N.

Yellow-shade dyes are usually monoazo compounds from *ortho* coupling phenols or enolizable keto compounds, the latter class including a number of novel heterocyclic components besides the long-established pyrazolones. The Eastman Kodak Co.[112] describe yellow dyes of high tinctorial power obtained by coupling a 2-nitroaniline, which may have various substituents in the 4-position, with a 3-carbalkoxy- or 3-carbamyl-5-pyrazolone having H or alkyl in the 1 position, in particular the dye: 2-nitroaniline-4-sulphonyl-*n*-butylamide → 3-carbethoxy-5-pyrazolone (greenish-yellow). The same firm[113] use a 2 : 3 : 4 : 5-tetrahydro-1 : 2 : 4-thiadiazine-3 : 5-dione-1 : 1-dioxide (E^1) as coupling component for dyes for cellulose acetate rayon and nylon or, when the diazo component is sulphonated, for wool and silk, e.g. *p*-phenetidine → the 2 : 4-di-(2′-hydroxyethyl) derivative of E^1 (yellow). The General Aniline & Film Corporation[114] use 6-ethyl- (E^2) or-*n*-propyl-2 : 3-dihydro-1 : 4-pyran-2 : 4-dione as coupling component for yellow dyes for acetate rayon and as a developer for diazotizable dyes on the fibre, e.g. *m*-chloroaniline → E^2 is a greenish-yellow of excellent fastness to light and washing, and having good exhaustion and building-up properties. The Allied Chemical & Dye Coporation[115] use 6-amino-1 : 3-benzdioxan (A) as diazo component for dyes fast to washing and sea water, e.g. A → phenol (yellow).

The Eastman Kodak Co. have continued their investigation of heterocyclic coupling components (E) containing a N atom in the heterocyclic ring which directs coupling to the corresponding *para* position in a fused benzo ring. The diazo compound is generally a 4-nitroaniline optionally substituted in the 2- and 6-positions with various groups. Thus E can be a 3 : 4-dihydroxy-2 : 2′-dialkyl-1 : 2 : 3 : 4-tetrahydroquinoline, in particular for the blue: 2 : 4-dinitroaniline-6-sulphonylethylamide (A) → 3 : 4-dihydroxy-2 : 2 : 4 : 7-tetramethyl-1-2′ : 3′-dihydroxypropyl-1 : 2 : 3 : 4-tetrahydroquinoline[116]; or E is a trifluoromethyltetrahydroquinoline or -benzmorpholine, e.g. as in the blue: A → 2-methyl-7-trifluoromethyl - 1 - 2′ : 3′-dihydroxypropyl - 1 : 2 : 3 : 4-tetrahydroquinoline[117]; or E is a 4 : 5-trimethylenebenzmorpholine as in the rubine: *p*-nitroaniline → 2′-hydroxy-3 : 1′-dimethyl-4 : 5-1′ : 3′-trimethylenebenzmorpholine[118]; or E is a 1 : 2 : 3-benz- or -naphtho-triazole as

in the blue: 6-chloro-2 : 4-dinitroaniline → 6-acetylamino-1-2′ : 3′-dihydroxypropyl-1 : 2 : 3-benztriazole.[119] The Eastman Kodak Co.[120] also use coupling components m-X·C_6H_4·NRR', where X is H, alkyl, or halogen, R is CH_2·CH_2·CO·OMe or CHMe·CH_2·COMe, and R' is hydroxyalkyl (2-3C) or R, for dyes such as *p*-nitroaniline → *N*-2-hydroxyethyl-*N*-1′-methyl-2′-carbomethoxyethylaniline.

Imperial Chemical Industries Ltd.[121] have described further water-soluble dyes having good affinity for cellulose acetate rayon when dyed from the dilute liquors used in winch machines. They are disazo dyes giving orange shades of the pattern: *m*- or *p*-aminophenyl hydroxyalkyl ether sulphuric ester → *para*-coupling benzenoid or naphthalenoid amine → a phenol having a hydrocarbon radical (C > 3) in the 2-position, e.g. *p*-aminophenyl 2-hydroxyethyl ether sulphuric ester → α-naphthylamine → *o*-hydroxydiphenyl.

A disazo dye of Eastman Kodak Ltd.[39] which dyes cellulose acetate rayon in rose shades has the constitution: *NN′*-bis-*m*-aminobenzenesulphonyl-*NN′*-dimethyl-*p*-phenylenediamine $\overset{\text{acid}}{\rightrightarrows}$ (1-2′ : 3′-dihydroxypropylamino-5-naphthol)$_2$; wool dyes from similar diamines are mentioned earlier in this review.

In the field of diazotizable colours, Manufactures de Produits Chimiques du Nord Etablissements Kuhlmann[122] use nitroaminoazo compounds of constitution: 5 : 2 : 1 : 4-X·$C_6H_3(NO_2)(NH_2)$·N_2·C_6H_4·NRR'-1′ : 4′, where X is H, halogen, alkyl, or alkoxy, R and R' are alkyl or hydroxyalkyl, and the benzene nucleus devoid of NO_2 may contain other substituents, principally for diazotization and development on the fibre with 2-hydroxy-3-naphthoic acid to give brown shades. The azo compounds are prepared by monodiazotizing a 2-nitro-1 : 4-phenylenediamine and coupling with the appropriate tertiary amine, e.g. 2-nitro-1 : 4-phenylenediamine→*NN′*-di-(2-hydroxyethyl)aniline which gives an olive-brown shade on development.

Lakes and pigments

There is little to report concerning azo pigments. Imperial Chemical Industries Ltd.[123] obtain a bright yellowish-red pigment for colouring rubber, polyvinyl chloride, etc., by coupling tetrazotized 3 : 3′-dichlorobenzidine containing 5–20% of tetrazotized dianisidine with 2 mols. of 1-*p*-tolyl-3-methyl-5-pyrazolone. The General Aniline & Film Corporation[124] use a 4-cyano-2 : 5-dialkoxyacetoacetanilide as coupling component for yellow pigments obtained in substance or on the fibre with diazo compounds such as 5-chloro-*o*-toluidine, etc. The Interchemical Corporation[125] convert relatively light-sensitive pigments to ones of high light-fastness by reacting them in dispersion under alkaline conditions with an excess of a copper salt, e.g. the orange 3 : 3′-dichlorobenzidine $\rightrightarrows$ (1-phenyl-3-methyl-5-pyrazolone)$_2$ is converted by this means to a khaki pigment. The brilliant bluish-red barium lake of *p*-toluidine-3-sulphonic acid → β-naphthol described by E. I. Du Pont de Nemours & Co.[126] is specially suitable for printing inks owing to its excellent resistance to bleeding in both water and oils.

References

[1] Hodgson, H. H. and Norris, W. H. H., *J. Soc. Dy. Col., Bradford*, 1949, **65**, 226
[2] de Jonge, J. and Dijkstra, R., *Rec. Trav. chim. Pay-Bas*, 1948, **67**, 328
[3] Süs, O., *Ann. Chem.*, 1944, **556**, 65, 85; cf. Annual Reports, 1946, **31**, 106
[4] Grimmel, H. W. and Morgan, J. F., *J. Amer. chem. Soc.*, 1948, **70**, 1750
[5] Hodgson, H. H. and Norris, W. H. H., *J. chem. Soc.*, 1949, 87
[6] Porai-Koshits, B. A. and Grachev, I. V., *J. gen. Chem., Moscow*, 1946, **16**, 571
[7] Idem, ibid., 1947, **17**, 1843
[8] Grachev, I. V., ibid., 1834
[9] Idem, ibid., 2268
[10] Grachev, I. V. and Shour, V. M., ibid., 1948, **18**, 1179
[11] Grachev, I. V., ibid., 838
[12] Idem, ibid., 848
[13] Bami, H. L., *J. Indian Inst. Sci.*, 1948, **30A**, 15
[14] Idem, *Curr. Sci.*, 1948, **17**, 186
[15] Morgan, J. F., *J. Amer. chem. Soc.*, 1948, **70**, 2253
[16] Eastman, R. H. and Detert, F. L., ibid., 962
[17] U.S.P. 2,441,800, 2,474,779–80
[18] Gochenour, C. I. and Degering, E. F., *Proc. Indiana Acad. Sci.*, 1948, **57**, 88; *Chem. Abs.*, 1949, **43**, 4646
[19] Parkes, G. D., *J. chem. Soc.*, 1948, 2143
[20] Polonovski, M. and Pesson, M., *Bull. Soc. Chim. Fr.*, 1948, [V], **15**, 688
[21] Porai-Koshits, B. A. and Efros, L. S., *J. gen. Chem., Moscow*, 1948, **18**, 929
[22] Ufimtsev, V. N., *J. appl. Chem., U.S.S.R.*, 1947, **20**, 1283
[23] Raman, V. V. and Sitaraman, M. V., *Curr. Sci.*, 1949, **18**, 44
[24] Löb, W., *Z. Elektrochem.*, 1904, **10**, 237
[25] Pearl, I. A. and Ronzio, A. R., *J. org. Chem.*, 1947, **12**, 785
[26] Lukashevich, V. O. and Kurdyumova, T. N., *J. gen. Chem., Moscow*, 1948, **18**, 1963
[27] Wang, A. B. and Yuen, C. Y., *J. Chin. chem. Soc.*, 1948, **15**, 215
[28] Bennett, H. S. and Yphantis, D. A., *J. Amer. chem. Soc.*, 1948, **70**, 3522
[29] Schwarzenbach, V. and Biedermann, W., *Helv. chim. Acta*, 1948, **31**, 678
[30] Wiley, R. H. and Smith, N. R., *J. Amer. chem. Soc.*, 1948, **70**, 2295
[31] B.P. 622,935
[32] U.S.P. 2,447,440
[33] Fusco, R. and Romani, R., *Gazz. Chim. Ital.*, 1946, **76**, 419
[34] Idem, ibid., 1948, **78**, 332
[35] Wizinger, R. and Biro, V., *Helv. chim. Acta*, 1949, **32**, 901
[36] B.P. 621,642
[37] B.P. 616,507
[38] B.P. 617,799
[39] U.S.P. 2,448,853
[40] B.P. 614,191
[41] B.P. 626,916
[42] B.P. 624,247
[43] B.P. 615,606
[44] B.P. 610,857, U.S.P. 2,447,164
[45] U.S.P. 2,459,813
[46] B.P. 609,039
[47] U.S.P. 2,447,867
[48] U.S.P. 2,446,662
[49] U.S.P. 2,474,024
[50] B.P. 618,007
[51] Cf. B.P. 352,956 (I.G. Farben. A.-G.)
[52] U.S.P. 2,437,699
[53] B.P. 608,115
[54] B.P. 597,130
[55] B.P. 613,939
[56] B.P. 615,210
[57] B.P. 628,028
[58] Krähenbühl, E., *Text. Rdsch.*, 1949, **4**, 157
[59] B.P. 609, 301
[60] Cf. B.P. 102,881 (Society of Chemical Industry in Basle)

[61] Cf. also U.S.P. 2,424,066, 2,426,977, 2,427,537, 2,439,153, 2,476,259 and 2,476,260, which have similar subject matter
[62] B.P. 609,299
[63] B.P. 609,300
[64] B.P. 609,302
[65] B.P. 616,115
[66] Cf. B.P. 455,274
[67] B.P. 594,325
[68] B.P. 597,414; U.S.P. 2,427,534
[69] B.P. 604,921
[70] BIOS Final Report 1548, p. 106
[71] B.P. 629,412
[72] B.P. 627,069
[73] B.P. 614,652
[74] B.P. 620,257
[75] U.S.P. 2,394,114
[76] BIOS Final Report 1548, p. 119
[77] B.P. 610,772
[78] B.P. 612,174
[79] B.P. 624,018
[80] B.P. 595,181
[81] B.P. 616,523
[82] B.P. 603,267
[83] B.P. 595,491; cf. ANNUAL REPORTS, 1948, **33**, 84
[84] B.P. 601,266; U.S.P. 2,460,618
[85] B.P. 619,688
[86] B.P. 616,977
[87] B.P. 606,872
[88] B.P. 602,254
[89] B.P. 601,369; cf. ANNUAL REPORTS, 1948, **33**, 85
[90] B.P. 604,690
[91] B.P. 616,950
[92] B.P. 623,913; U.S.P. 2,458,776
[93] B.P. 619,373
[94] U.S.P. 2,448,158
[95] B.P. 622,941
[96] B.P. 608,897
[97] U.S.P. 2,436,697, 2,437,644
[98] U.S.P. 2,427,995
[99] U.S.P. 2,419,334
[100] U.S.P. 4,426,567
[101] B.P. 603,753
[102] U.S.P. 2,465,979, 2,468,457
[103] U.S.P. 2,468,600
[104] B.P. 598,985–6
[105] B.P. 613,130; U.S.P. 2,419,932
[106] B.P. 599, 834
[107] Petitcolas, P. and Sureau, R., *Teintex*, 1948, **13**, 111
[108] B.P. 611,320
[109] B.P. 611,321
[110] Lantz, R., *Bull. Soc. chim. Fr.*, 1948, 489
[111] Idem, *Teintex*, 1948, **13**, 191
[112] U.S.P. 2,439,798
[113] U.S.P. 2,466,397
[114] B.P. 623,763
[115] U.S.P. 2,468,277
[116] U.S.P. 2,448,871
[117] U.S.P. 2,442,345
[118] U.S.P. 2,448,869
[119] U.S.P. 2,448,870
[120] U.S.P. 2,470,094
[121] B.P. 609,275; cf. ANNUAL REPORTS, 1948, **33**, 90

[132] B.P. 613,110
[133] B.P. 621,599
[134] U.S.P. 2,453,692
[135] U.S.P. 2,454,266
[136] U.S.P. 2,453,490

ANTHRAQUINONE DYES, PHTHALOCYANINES AND MISCELLANEOUS DYES (J. Wardleworth, M.Sc.)

Anthraquinone dyes

Acid wool dyes

ACTIVITY in this field, judged from the number of publications, has been small during the current period, and developments have followed familiar lines.

Bezzubets and Rozina[1] have investigated the effect on fastness properties of substituting Cl and Me in the anilino-residue of 1-amino-4-arylaminoanthraquinone-2-sulphonic acids; the absorption maxima of solutions of the sodium salts of the dyes are also reported.

The Allied Chemical and Dye Corpn.[2] describe dyes for nylon, wool, etc., giving blue to green shades from acid or neutral baths, obtained by condensation of a 1-halogenoanthraquinone, carrying a N*RR'* group at position 4 (*R* and *R'* may be H, alkyl or substituted alkyl, aryl or heterocyclic radicals, etc.), and optionally substituted by CO_2H or SO_3H at position 2, with amino- or diamino-derivatives of heterocyclic *o*-diphenylene compounds, e.g. carbazole, dibenzfuran, dibenzthiophen, which may also carry alkyl, alkoxy, aryl, halogen or sulpho groups. Metallic lakes (Ba, Al, Mg, Cu) of the above compounds are said to give bright and clear shades.

Blue dyes for wool, silk and nylon are prepared, according to Sandoz Ltd.,[3] by sulphation of anthraquinones containing hydroxyalkylamino-groups at positions 1 and 4 and halogen at 6 and/or 7.

Imperial Chemical Industries Ltd. have a number of patents in this field. They make blue wool dyes, probably of the same constitution as examples of earlier patents,[4,5] by condensation of an amine, NH_2·CH*RR'* (where *R* is a sulphonated aryl or aralkyl residue, and *R'* is a hydrocarbon radical which may be linked with *R* in a *cyclo*aliphatic ring, both optionally substituted further), with a leuco-1 : 4-dihydroxy- or 1-hydroxy-4-amino- (or -alkyl-amino-)anthraquinone, which may carry hydroxy groups at 5 and/or OH or halogen at 6 and/or 7.[6] Fast violet dyes are made[7] by sulphonating the product obtained by condensing 2 : 3-dichloro-1 : 4-diaminoanthraquinone with an alkali metal salt of a *p*-phenyl- or *p*-phenoxy-phenol or 3-hydroxydibenzfuran, whilst sulphonation of 6-phenylazoanilino-1' : 9'-anthrapyridaz-3-ones, optionally substituted at 2 by aryl groups, or further substituted in the phenylazoanilino residue, affords[8] orange wool dyes of high light-fastness. An improved method of preparing 1-, 5-, or 8-acylamino-4-*p*-phenylazonanilinoanthraquinone sulphonic acids, which dye wool in clearer and brighter shades than the previously described[9] products, which consists of acylation of the amino-group after carrying out the sulphonation, is described by the same inventors.[10]

Dyes for cellulose esters

The volume of patent literature shows a slight increase in activity in this field particularly in the U.S.A.; as usual, the main objective has been the production of colours fast to acid (gas-fume) fading, mainly in the blue range.

The Allied Chemical and Dye Corpn.[11] alkylate aminoanthraquinones, preferably of the 1, 4, 6 and 7 types, by treatment with an aldehyde and $(COOH)_2$, the latter acting as a condensing and reducing agent, and in some cases effecting desulphonation; thus Alizarin Sapphire (C.I.1054), which is mainly 4 : 8-diamino-1 : 5-dihydroxyanthraquinone-2 : 6-disulphonate, is treated with CH_2O and $(COOH)_2$ to give a greenish-blue dye consisting of a mixture of 4 : 8-di-methylamino-1 : 5-dihydroxyanthraquinone-2 : 6-di- and -2-sulphonic acids. Two patents[12,13] by the Celanese Corpn. of America follow similar lines: leuco-anthraquinones containing amino groups, e.g. leuco-4 : 8-diaminoanthraquinone or -anthrarufin, are alkylated with an aliphatic aldehyde alone,[12] or aminohydroxyanthraquinones, e.g. 2-amino-1 : 4 : 5 : 8-tetrahydroxyanthraquinone, are similarly alkylated in presence of a catalyst, e.g. $CuCl_2$,[13] giving compounds of greenish-blue shade useful for vat or suspension dyeing of cellulose derivatives.

The Society of Chemical Industry in Basle have published a series of patents on blue to green dyes. Fast-to-light blues are obtained[14] from 4-halogeno-1-aminoanthraquinones containing halogen or sulpho at position 2, by reaction first with aniline, *p*-aminophenol or *p*-phenylenediamine, then with an alkali metal sulphide to give the 2-thiol, which is alkylated by a halohydrin containing not more than 6 C atoms; e.g. 2-bromo-1-amino-4-anilinoanthraquinone is treated with NaHS, and then with glycerol chlorohydrin, to give 1-amino-4-anilino-2-(2′ : 3′-dihydroxypropylthio)anthraquinone. The above products are converted[15] into water-soluble derivates by treatment with an inorganic acid, e.g. H_2SO_4 giving the sulphate, or by reaction with a dicarboxylic acid (e.g. maleic, succinic, phthalic) or a functional derivative, so as to leave a free COOH, capable of conversion into a water-soluble salt. A similar reaction is utilized[16] for the solubilization of anthraquinones containing not less than 2 NH_2 groups, by treatment with dicarboxylic anhydrides. Navy Blue dyes are obtained[17] by replacement of one negative group in dinitro- or dihalogenodihydroxyanthraquinones by an amine, the second being subsequently converted into NH_2; e.g. the crude product obtained by dinitration of mixed 1 : 5-and 1 : 8-dihydroxyanthraquinones or derivatives is reacted, first with aniline, then with NaHS, giving a monoamino-monoanilino-dihydroxyanthraquinone.

The Eastman Kodak Co. extend the use of alkoxyaminoanthraquinones in two publications. The first[18] prepares blue anthraquinones having one hydroxyalkylanilino- and one alkoxyalkylamino-group; e.g. quinizarin with a mixture of monoethanolamine and 2-methoxy*iso*propylamine affords 1-(2′-hydroxyethylamino)-4-(2″-methoxy*iso*propylamino)anthraquinone. The second[19] describes dyes, fast to gas fumes, consisting of anthraquinones having a group NH*R*′ (*R*′ is an alkyl, alkoxyalkyl or hydroxyalkyl containing not more than 4 C) in position 1 and a group

NH·*Q*·(O*D*)$_n$·O*R* (where *D* is $(CH_2)_2$ or $_3$ or propylene, *R* is H, Me or Et, *Q* is an *o*- or *p*-phenylenediamine residue and *n* is 2 or 3) at 4, e.g. 1-[4′ - (2″ - hydroxyethoxyethoxyethoxy)anilino] - 4 - methylaminoanthraquinone.

The condensation of haloquinizarins with NH_3 or amines affords, according to Sandoz Ltd.,[20] dyes having good light fastness on cellulose acetate, also useful for the coloration of organic solvents, e.g. 6-chloro-1 : 4-diamino- (violet), 6-chloro-1 : 4-dimethylamino- (blue), 6 :7-dichloro-1 : 4-diamylamino-anthraquinone (greenish-blue).

British Celanese Ltd.[21] claim the preparation of 1-hydroxy-4-alkylamino-, -arylamino- or -aralkylamino-2 : 3-dicyanoanthraquinones by reaction of the 1-hydroxy-4-substituted aminoanthraquinone-2-sulphonic acids with aqueous alkali cyanides. The products are blues fast to gas fumes.

The same company[22] prepare red-violet dyes of good fastness to light and gas fumes by condensation of a 1-amino-4-*o*-alkylanilinoanthraquinone-2-sulphonic acid with $CH_2Ac·CO_2Et$ giving 3′-acetyl-4-*o*-alkylanilino-1 : 9-anthrapyridone-2-sulphonic acids.

Vat dyes

Novelty is again lacking in this field, the work being concerned mainly with the extension of well-established themes.

Müller[23] discusses the influence of various factors on keto–enol tautomerism in the leuco compounds of vat dyes, especially the effect of NaOH concentration, and indicates the anomalies to be expected during dyeing.

The Society of Chemical Industry in Basle have further exploited the use of benzoyl chlorides carrying sulphonyl residues. Thus,[24,25] 1 : 4-dibenzamidoanthraquinones in which at least one benzamido group has a SO_2Aryl residue are described; the other benzamido residue may carry Cl, OMe or Me, and the anthraquinone nucleus may be substituted by halogen. Vattable amines are also acylated[26] with benzoic acids containing sulphamyl groups, e.g. SO_2·NMe$_2$, SO_2·NHEt, SO_2·NPhMe etc., to give valuable dyes; thus are prepared 1-benzamido-4-*p*-*NN*-dimethylsulphamylbenzamido- (pink), 1 : 4-di-(*p*-*N*-methylsulphanilylbenzamido)-anthraquinone and 3-*p*-*NN*-diethylsulphamylbenzamido-1 : 2-phthaloylacridone (greenish-blue). In the preparation of more complex dyes, e.g. anthrimides, the intermediates may be acylated with acids of the above type, before condensation with further reactants.

The use of chlorinated benzoic acids for the acylation of vattable amines originates from the same source. 1 : 5-Di(*p*-halogenobenzamido)-anthraquinone, or an isomeric mixture consisting mainly of the above, is said to yield fast yellow tints on cotton,[27] whilst 3-*p*-halogenobenzamido-1 : 2-phthaloylacridones are prepared by cyclization of 4-*p*-halogenobenzamido-1-*o*-carboxyanilinoanthraquinones.[28] Ring closure of a 1-amino-5-(3′-*meso*-benzanthronylamino)anthraquinone, followed by acylation with *o*-chloro-, *o*-bromo-, or 2 : 4-dichloro-benzoylchloride affords olive vat dyes of excellent fastness.[29] The products may be converted into leuco-ester salts or can be subsequently halogenated. The shades obtained are purer than those of the dyes made by halogenating the corresponding benzamido compounds.

Sandoz Ltd.[30] acylate vattable anthraquinones containing at least one primary NH_2 group with the acid chloride of a 1-benzamido-4-*p*-carboxyanilinoanthraquinone; e.g. 1-amino-5-benzamidoanthraquinone with the acid chloride of 1-benzamido-4-*p*-carboxyanilinoanthraquinone affords an olive vat dye. The products are stated to have high fastness to Cl_2 and Na_2CO_3.

5-Amino-1 : 4-diaroylaminoanthraquinones are employed by Imperial Chemical Industries Ltd.; acylation with an anthraquinone-2-carboxylic acid carrying at position 1 an NH_2 group or a group capable of conversion into NH_2 affords Bordeaux vat dyes,[31] whilst condensation of 2 mols. or more with cyanuric halides, the residual halogen, if any, being condensed with NH_3 or a primary or secondary amine, yields bluish-red dyes.[32]

The same firm[33] prepare a yellow-olive dye of high fastness to light and soda boil, by acylation of 2-amino-3-hydroxyanthraquinone with 1-bromonaphthalene-4-carbonyl chloride, cyclization to the oxazole, and condensation of the product with 3-amino-1 : 2-phthaloylacridone.

Condensation of a vattable amine (e.g. 1-amino-4-methoxyanthraquinone, an aminoanthra-pyrimidine or -dibenzanthrone) with a halogenobenzanthrone (e.g. 1-bromo*meso*benzanthrone), followed by cyclization with strong alkali gives, according to General Aniline and Film Corpn.,[34] olive to brown dyes, stable to Cl_2.

E. I. Du Pont de Nemours & Co.[35] interact amino- and halogenoanthraquinones in absence of solvent, by heating with an acid-binding agent and a catalyst whilst grinding the reactants in a roller mill, thus obtaining anthrimides, which on treating with aluminium chloride and an alkali metal salt in similar apparatus give the carbazoles.[36]

Orange-yellow anthrimide-carbazoles are obtained, by the American Cyanamid Co.,[37] by ring-closure of the anthrimides in a high-boiling solvent with aluminium chloride in presence of a nitro compound containing solubilizing groups (e.g. Na *m*-nitrobenzenesulphonate or Na *p*-nitrophenate). The same company[38] prepare fast dyes giving, e.g. olive-drab shades, by $AlCl_3$-cyclization of pentanthrimides, e.g. 1'':4'-1':1-4:1'''-8:1''''-pentanthrimide, obtained by condensation of 1-chloro-8-nitro- and 1-amino-anthraquinones, nitration and reduction to the triamino-1 : 1'-dianthrimide, and condensation with 1-chloroanthraquinone.

General Aniline & Film Corpn.[39] condense a 6-chloro-3-benzamido-1 : 2-phthaloylacridone with a 1-aminoanthraquinone optionally substituted at 4- and/or 5- by NH·CO*R* or *OAlk*, and cyclize the product to obtain olive anthrimide-carbazole-acridones, e.g. 3''-benzamido-1'' : 2''-phthaloylacridono-7'' : 6''-4 : 5-(anthraquinono-1' : 2'-2 : 3-)pyrrole.

E. I. Du Pont de Nemours & Co.[40] employ oxidative ring-closure for the preparation of dibenzanthrones from 2 : 2'-dibenzanthronyl and derivatives. The reaction is carried out in 80–90% H_2SO_4 in presence of, e.g. $NaNO_2$ or As_2O_3.

In the field of leuco-sulphuric esters of vat dyes of the anthraquinone and indigo series, Imperial Chemical Industries Ltd.[41] have made an important contribution in eliminating the use of pyridine and related compounds as solvents. Treatment of the vat dye with sulphating agents and a metal (e.g. Fe, Ni, Cu, brass), in a solvent of the type, *R*CO·N*R'R''* (where R = H or an organic radical and R' and R'' are the same or

different hydrocarbon radicals), e.g. dimethylformamide, diethylacetamide, tetramethylurea, *N*-methylphthalimidine, yields the required ester. The same firm also have a patent[42] for the preparation of leuco-sulphuric esters of 1 : 4-dibenzamidoanthraquinones, by reaction with Cu or an alloy in presence of SO_3, a cuprous salt and a tertiary base.

Durand and Huguenin[43] employ quaternary salts from tertiary alkylolamines containing ether linkages to aid in the dispersion of leuco-sulphuric esters. They also prepare leuco-sulphuric esters of anthraquinoneazo dyes of the type 1-aminoanthraquinone $\rightarrow$ $C_6H_4Ph.CO.CH_2.CO.NHR$ (where R is aryl substituted by H, alkyl, alkoxy or aroylamino) by reaction with a metal (e.g. Fe), a substance yielding SO_3 (e.g. $ClSO_3H$), and a tertiary base (e.g. pyridine).

The chloromethylation of dyes (ANNUAL REPORTS, 1948, **33**, 100) has now been extended by Imperial Chemical Industries Ltd. to the anthraquinone field. Thus derivatives of acedianthrone[44] and dibenzanthrone[45] are prepared, and the products converted to water-soluble dyes by reaction with thiourea and its alkyl derivatives,[46] with tertiary bases (e.g. pyridine, triethylamine)[47] or by formation of an alkali metal mercaptide and subsequent treatment with an ester (e.g. dimethyl sulphate, methyl *p*-toluenesulphonate) to give ternary sulphonium salts.[48] The solubilization of chloromethyl derivatives of simpler structure, e.g. anilino- or phenyl-anthraquinones, anthra-pyridones and -pyrimidines is also covered.

Phthalocyanines

E. I. Du Pont de Nemours & Co.[49] employ SCl_2 in presence of $FeCl_3$ and/or $SbCl_3$ for the production of phthalocyanines containing about 50% Cl.

Phthalocyanines carrying substituted sulphonyl groups are described by the General Aniline & Film Corpn. A phthalocyanine sulphonyl chloride is reacted (*a*) with a polyhydroxy primary alkylamine[50] to give fast blue to greenish-blue dyes (e.g. copper phthalocyaninetetrasulphonyl chloride and aminotri(hydroxymethyl)methane yields a vivid greenish-blue dye for cotton, wool or silk), (*b*) with hydrazine or its derivatives containing at least one free NH group[51] to give pigments or dyes for cotton, wool and silk, or (*c*) with 2-, 3- or 4-aminopyridines[52] to obtain brilliant blue dyes for cotton, wool or silk, having greater solubility in water or dilute sodium hydroxide solution than the products derived from other heterocyclic amines.[53] If free SO_3H groups are present, the compounds can be made into lakes (e.g. Ca or Ba) suitable for colouring inks.

Imperial Chemical Industries Ltd.[54] describe a further route to water-soluble sulphonium salts of phthalocyanines. A phthalocyanine containing not less than 2 halogenomethyl groups is treated with a thiourea, hydrolysed by alkali to the sodium thiol, alkylated and then reacted with an ester to give a ternary sulphonium salt useful for dyeing cotton in fast blue shades.

Miscellaneous dyes

The volume of publications in this class shows some increase, but little of novelty has appeared.

Further dyes of the nitrodiphenylamine type are described by the

Celanese Corpn. of America,[55] who obtain yellows for cellulose acetate, fast to acid and light, by condensation of 2-chloronitrobenzene-5-sulphonic acid with a 4-alkylaniline.

Hodgson[56] explains the colour of aminocoumarins in terms of modern resonance theory. Bird[57] has investigated the dyeing properties of aminoacridines; the 5-amino-compounds exhibit better fastness to light and wet treatments than most basic dyes.

New oil-soluble dyes to improve the appearance of lubricating oils and for the coloration of plastics comprise, according to American Cyanamid Co.,[58] 4-alkylamino-*N*-alkyl-1 : 8-naphthalimides in which one alkyl group contains not less than 12 C, and the other less than 6 C; e.g. 4-bromonaphthalic anhydride is reacted with butylamine, then with octadecylamine, to give 4-octadecylamino-*N*-butylnaphthalimide.

Sandoz Ltd.[59] prepare intermediates or dyes by the condensation of halogenonaphthaquinoneimides with NH_3, amines, polyhydric alcohols, ether alcohols, phenols or thiophenols.

The constitution of the primuline dyes, Immedial Yellow GG and Immedial Orange, has been elucidated by Zerweck, Ritter and Schubert,[60] and the commercial products matched satisfactorily by synthetic mixtures of known formulation.

E. I. Du Pont de Nemours & Co.[61] sulphurize dyes and pigments of the anthraquinone (thio)indigo, azo, phthalocyanine and sulphur series by treatment with a complex (e.g. $AlCl_3$, $2S_2Cl_2$), thus obtaining dyes for cotton, silk, wool, rayon and nylon.

Aminophthalimides for use as fluorescent dyes for artificial and natural fibres are produced, by the American Cyanamid Co.,[62] by condensing a nitrophthalic acid with an amino alcohol, dehydrating to the imide, reducing the NO_2 group and optionally alkylating the NH_2 thus formed; examples include 3-heptylamino-*N*-octadecyl-, 3-chloro-6-*N*-2′-hydroxyethylamino-*N*-2′-hydroxyethyl-, and 3-heptylamino-*N*-2′-hydroxyethylphthalimide.

Imperial Chemical Industries Ltd.[63] prepare 2-(1″ : 4″-dichloro-4 : 5-benzindole)-2′-(4′ : 5′-benzthionaphthen)indigo, a dark brown for cotton or viscose, of excellent fastness properties, and notably stable to variation in conditions of soaping unlike other browns of this type, by interaction of 1′ : 4′-dichloro-4 : 5-benzisatin and 4 : 5-benzthionaphthen-3-ol in presence of a nitrogenous base.

Further examples of the thioindigoid series are described by the Society of Chemical Industry in Basle.[64] 3′ : 6′-Dihalogeno-3-hydroxybenz-1′ : 2′-6 : 7-thionaphthen or a reactive 2-derivative is condensed with a 2-(*p*-dimethylaminoanilo)thionaphthenquinone, an isatin or an acenaphthenequinone; e.g. 3′ : 6′-dichloro-3-hydroxybenz-1′ : 2′-6 : 7-thionaphthen (prepared from 5 : 8-dichloro-1-aminonaphthalene, by conversion to the 1-thiol, the 1-thioglycollic acid and ring closure) with 2-(*p*-dimethylaminoanilo)thionaphthenquinone affords a garnet dye.

Acid dyes (e.g. Naphthol Green B, Patent Blue A, Nigrosine WS, Alizarine Cyabine Green, etc.) are converted into oil-soluble colours, by the American Cyanamid Co.,[65] by treatment with an ester of a high molecular weight fatty acid (e.g. oleic, stearic, lauric, soya bean oil), and the condensation product of a trialkylolamine and an alkylene oxide.

In the field of triarylmethane dyes, Ballio[66] describes the use of $HgCl_2$ in their preparation, whilst the General Printing Ink Corpn.[67] oxidize 2-dimethylaminodiphenyl, containing a little 2-methylamino compound, in presence of $CuSO_4$, H_2O and phenol, and add NaOH to give a triarylmethane base, which is used in oleic acid solution as a paint or printing ink colour, for the production of pigments when laked with phospho-tungstic or -molybdic acids, etc., or as the hydrochloride for dyeing cotton, wool and silk in violet-blue shades.

Methine dyes are obtained, according to the Society of Chemical Industry in Basle,[68] by reaction of cyanacetic esters or amides with *N*-alkyl-*p*-aminobenzaldehydes, and subsequent treatment with maleic anhydride or sulphuric acid, if desired. The products dye cellulose derivatives, polyamides and polyurethanes. A similar reaction, the condensation of a *p*-dialkylaminobenzaldehyde with a reactive methylene compound, e.g. malononitrile, cyanacetic ester, *N*-methyloxindole, is used by General Aniline & Film Corpn.[69] for the production of polymethine dyes for cotton and cellulose derivatives.

Imperial Chemical Industries Ltd.[70] prepare colours of the azomethine type, for paper, cellulose acetate, nylon, etc., by condensation of imino-, thio- or iminothio-phthalimidines or their nuclear substituted derivatives with aromatic hydrazines or primary amines containing a further NH*R*, $NH{\cdot}NH_2$ or condensed or pendant ring; e.g. iminophthalimidine and dehydrothio-*p*-toluidine or *o*-dianisidine give yellow dyes.

References

1 *J. appl. Chem., U.S.S.R.*, 1948, **21**, 1152
2 B.P. 610,808
3 U.S.P. 2,386,309
4 B.P. 497,016
5 B.P. 564,859
6 B.P. 609,585
7 B.P. 619,034
8 B.P. 615,837
9 B.P. 560,988
10 B.P. 604,833
11 U.S.P. 2,443,899
12 U.S.P. 2,368,681
13 U.S.P. 2,368,682
14 B.P. 607,955; U.S.P. 2,434,765
15 B.P. 607,956; U.S.P. 2,441,355
16 U.S.P. 2,392,663
17 B.P. 612,009
18 U.S.P. 2,398,454
19 B.P. 626,704
20 U.S.P. 2,433,551
21 B.P. 614,969
22 B.P. 613,319
23 *Melliand Textilber*, 1947, **28**, 136, 273
24 B.P. 605,701
25 U.S.P. 2,439,626
26 B.P. 605,466
27 B.P. 604,916
28 B.P. 604,981
29 B.P. 613,836
30 U.S.P. 2,374,891
31 B.P. 603,317

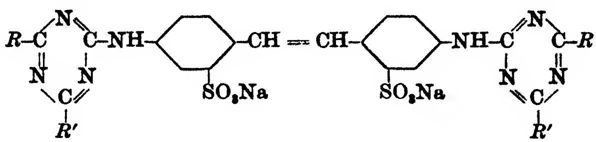
[32] B.P. 602,975
[33] B.P. 611,786
[34] U.S.P. 2,392,794
[35] B.P. 603,495
[36] B.P. 603,496
[37] U.S.P. 2,432,972
[38] U.S.P. 2,385,113
[39] B.P. 620,782
[40] U.S.P. 2,388,743
[41] B.P. 610,117
[42] B.P. 605,617
[43] U.S.P. 2,388,285
[44] B.P. 612,222
[45] B.P. 623,998
[46] B.P. 613,980
[47] B.P. 613,982
[48] B.P. 613,984
[49] U.S.P. 2,377,685
[50] B.P. 613,781
[51] B.P. 613,782
[52] B.P. 614,407
[53] Cf. B.P. 520,199
[54] B.P. 619,035
[55] U.S.P. 2,443,666
[56] *J. Soc. Dy. Col., Bradford*, 1949, **65**, 14
[57] Ibid., 357
[58] U.S.P. 2,385,106
[59] B.P. 613,076
[60] *Angew. Chem.*, 1948, **60A**, 141
[61] U.S.P. 2,369,666
[62] U.S.P. 2,436,362
[63] B.P. 619,357
[64] B.P. 607,608
[65] U.S.P. 2,392,158
[66] *Gazz. Chim. ital.*, 1948, **78**, 358
[67] B.P. 614,391
[68] U.S.P. 2,374,880
[69] U.S.P. 2,385,747
[70] B.P. 615,697

COLOURLESS FLUORESCENT DYES—OPTICAL BLEACHING AGENTS (D. A. W. Adams, B.Sc., Ph.D.)

THE last few years have seen the commercial introduction of a number of colourless, fluorescent and substantive compounds which have the property of improving the whiteness of undyed materials by reason of their capacity for absorbing the ultra-violet light in daylight and re-emitting it as visual blue light. Such compounds have been termed 'optical bleaching agents.' The earliest products were the Blankophors of the I.G., and their development, manufacture and use are described in a FIAT report.[1] Reviews covering these and other similar compounds mentioned in patents have also recently appeared[2,3] and there seems to be a wide general interest in such compounds. They can be used in soap powders,[4] in discharge printing pastes,[5] and for treatment of cotton, wool, etc. and paper.

Many of the compounds of this type are derivatives of 4 : 4′-diamino-stilbene-2 : 2′-disulphonic acid in which the NH_2 groups are converted

into NH·CO·NHPh, NH·CO·C_6H_4·NH_2-*p*, NH·CO·C_6H_4·NH·CO·NH_2-*p*, etc. or are condensed with cyanuric chloride to give triazine compounds. Blankophor R, for example, is 4 : 4′-di-(*N*-phenylureido)stilbene-2 : 2′-disulphonic acid, whilst Blankophor B is the triazine derivative (I)



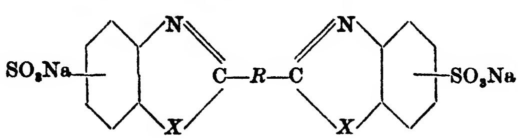
(I)

in which *R* is NHPh and *R′* is OH.[1] The rather similar compound made by treating the compound of type (I), in which *R* and *R′* are NH_2, with formaldehyde was mentioned in last year's report.[6]

Recent patents relating to stilbene derivatives cover modifications of these types in which improved whitening effects and/or increased stability to light are obtained by suitable choice of substituents. Thus, Imperial Chemical Industries Ltd. claim compounds of type (I) in which (*a*) *R* is NH·$[CH_2]_2$·OH and *R′* is Cl,[7] (*b*) *R* is N($[CH_2]_2$·OH)$_2$ and *R′* is Cl,[8] and (*c*) *R* is NH·$[CH_2]_2$·OH and *R′* is a substituted amino group such as NHPh, NH·C_6H_4·NHAc-*p*, NH·$[CH_2]_2$·OH, etc.[9] American Cyanamid Co.[10] extend the dibenzoyl-type to the 4 : 4′-di-(*o*-alkoxybenzamido)stilbene-2 : 2′-disulphonic acids, whereas Procter and Gamble[11] cover specifically 4 : 4′-di-(*p*-methoxybenzamido)stilbene-2 : 2′disulphonic acid.

A further variation is made by the Geigy Co., who cover stilbene derivatives in which one of the NH_2 groups is replaced by NH·CO·$(CH_2)_n$·O·*Ar* and the other (*a*) is replaced by a similar group or by NH·CO·*X*·*R*, where *X* is a direct linking, or O or NH, and *R* is alkyl or aryl[12] or (*b*) carries a triazine substituent as in type (I) above.[13]

Apart from the stilbene derivatives, most of the other fluorescent compounds described are representatives of type (II):



(II)

The compound of this type in which *R* is CH:CH and *X* is NH was referred to in the last report.[14] The group *R* can also be a *p*-phenylene nucleus or a furan nucleus joined at the 2- and 5-positions.[15] Variations can also be made in *X*; thus, one *X* can be O or S and the other NH, O, or S.[16] Unsulphonated compounds are also claimed[17]; a further variation is the compound obtained by condensing 2-methylbenziminazole with benzaldehyde-2 : 4-disulphonic acid.[18]

References

[1] FIAT Final Report, No. 1302

[2] Landolt, A., *Textil Rund.*, 1948, 3, 376

[3] Moncrieff, R. W., *Chem. Age*, 1949, **61**, 767 and 805
[4] Lever Bros., B.P. 584,484
[5] Imperial Chemical Industries Ltd., B.P. 508,205 (cf. ANNUAL REPORTS, 1947, **32**, 237)
[6] B.P. 598,985–6 (cf. ANNUAL REPORTS, 1948, **33**, 76)
[7] B.P. 623,849
[8] B.P. 624,051
[9] B.P. 624,052
[10] U.S.P. 2,468,431
[11] B.P. Appln. No. 29011/48
[12] B.P. Appln. No. 28215/48
[13] B.P. Appln. No. 27624/48
[14] B.P. 568,597 and B.P. 600,696 (cf. ANNUAL REPORTS, 1948, **33**, 76)
[15] Ciba Ltd., U.S.P. 2,463,264
[16] Idem, B.P. 623,428
[17] Idem, B.P. 611,510
[18] Idem, Swiss Pat. 238,842

FINE CHEMICALS AND MEDICINAL SUBSTANCES

BY MEMBERS OF THE FINE CHEMICALS GROUP

INTRODUCTION (H. J. Barber, Ph.D., F.R.I.C.)

May and Baker Ltd.

THE addition of the term 'Fine Chemicals' to the title of this section of the Report does not imply the intention to cover a wider range of topics. Indeed, there will be very few subjects or substances falling within the term 'Fine Chemicals' which will not already be grouped as medicinal substances or will not find more appropriate exposition in other sections. It is fitting, however, that the recent formation of the Fine Chemicals Group of the Society of Chemical Industry with the object, *inter alia*, of providing 'opportunities for the discussion of fine chemicals, especially those of therapeutic or biological interest' should find expression in the title of this section.

The main trend in medicinal chemistry has been towards 'symptomatics,' i.e. products for the alleviation of symptoms rather than for the cure of diseases produced by invading organisms. Thus Antihistamines constitute a prolific field of synthetic effort comparable with that of sulphonamides about 1940. 'Chloromycetin' and 'Cortisone' are probably the most interesting new developments in giving new leads for the future.

During 1949, in response to a request from the President of the Board of Trade, the Association of British Chemical Manufacturers carried out an enquiry into the status and plans of the different sections of the industries, together classed as the Chemical Industry. The report presented to the Board of Trade has been made public at a date too late for comments this year, but as in several respects its contents are of considerable relevance to the manufacture of fine chemicals, it is hoped to comment upon it next year, when it is likely to have gained from general discussion.

No report on medicinal substances would be complete without reference to the new British Pharmaceutical Codex 1949, which was published in October and followed the British Pharmacopoeia 1948, which appeared in September of that year. The changes that have been made in the contents of these two publications reflect some of the developments which have taken place in the Medicinals and Fine Chemicals Industry during the period, necessarily prolonged by the war years, since the B.P. 1932 and B.P.C. 1934. The trend from galenicals toward pure chemical substances, mainly synthetic, is naturally marked, but to give it quantitative expression by enumerating additions and deletions might be misleading. It could be inferred, for instance (from the fact that 28 tinctures remain in the B.P. 1948 against 34 in the B.P. 1932), that galenicals pass out of use only slowly. But some 25 synthetic organic medicinal substances have been added apart from about 40 introduced by the various addenda which bridged the 12-year gap ; there were less

than 30 in the B.P. 1932. The number of new substances of 'natural' origin is comparatively small though some, such as penicillin, are of supreme importance; the additions to the B.P.C. 1949 show the same trend. These comparisons alone would, however, imply a gross underestimate of the growth of the synthetic drug industry.

This progress is perhaps best conveyed by reference to a few selected representative substances in various groups introduced into the B.P. 1948: Sulphonamides: sulphathiazole, sulphadiazine, sulphaguanidine, sulphacetamide (sulphapyridine, introduced by the 7th Addendum in 1945, is now omitted); Barbiturates: pentobarbitone, thiopentone, hexobarbitone, phemitone (the B.P. 1932 included only barbitone and phenobarbitone); Steroid hormones: ethisterone, progesterone, testosterone propionate, oestradiol dipropionate; Antimalarials: mepacrine, pamaquin (proguanil is in the B.P.C. 1949); Organo-metallic substances: tryparsamide, carbarsone, sodium aurothiomalate; Vitamins: aneurine, calciferol, riboflavine, nicotinamide, ascorbic acid; aminacrine, dicoumarol, neostigmine, amphetamine, pethidine, thiouracil, ergometrine maleate.

It may be useful to refer to the General Medical Council's policy of Approved Names designed to reduce the number of names by which new medicinal substances are described. Suggested names may be submitted to the B.P. Commission for recognition as an Approved Name, but such approval does not imply that the substance will necessarily be included in the B.P. It is strongly recommended that any label shall bear the Approved Name of the substance at least as conspicuously as any proprietary name. The general principles on which the names are to be constructed have been given by the B.P. Commission.[1] An attempt should be made to form a name by the combination of syllables (not more than four) of the scientific chemical name in such a way as to indicate the significant groupings. It should therefore be free of any therapeutic or similar suggestion and be distinctive in sound and spelling from names already in use. Names already in the U.S.P., B.P.C., and New and Non-official Remedies (N.N.R.) are to be preferred. Terminal syllables should be systematic: -ine for alkaloids or bases, -in for glycosides, -ol for alcohols, phenols, -al for aldehydes, -one for ketones, -itone for barbiturates and -aine for analgesics. The urgency of the problem these measures are intended to solve is recognized by everyone.

Patents

Chemical patents and especially 'chemotherapeutic patents' have a potent influence in the Fine Chemicals and Medicinals industry. It must be made clear that it is not the purpose of this Report to examine essentially legal aspects or procedural matters, which are primarily the concern of patent agents and members of the patent bar. The intention is to report certain facts and to consider from the chemical standpoint some of their implications in so far as they appear likely to shape future progress and development. The Patents Act, 1949, came into force on January 1, 1950, and some of its provisions introduce far-reaching changes designed to promote reforms in the patent law especially in relation to chemical patents. The defects in the existing law and their remedies had been examined thoroughly by the Departmental Committee, set

up in 1945 under the Chairmanship of Mr. Kenneth Swan, K.C., which received evidence from interested parties, notably through the Joint Chemical Committee, on which were represented the A.B.C.M. and the leading chemical bodies. Their proposals, accepted in part, contributed materially to the results. The three reports of the Swan Committee,[2] indicative of the trend of opinion which would have a formative influence on the new law, and the Draft Consolidating and Amending Bill published in March, 1949, will have provided opportunity for the fine chemical industry to consider the possible effects on research and development policy.

The Act in its final form does not differ greatly from the Draft Bill, and probably the most important change in law is that it will now be possible to include as claims new chemical substances intended for food or medicine. Such claims had been specifically precluded by Section 38A introduced into the 1907 Act by the Patents and Designs Act of 1919. The 1949 Act omits this restriction in respect of substances intended for food or medicines. Thus it will be possible to claim new chemical substances as such (though these claims will not extend to the substances when found in nature [Section 4 (7)]) and not merely to claim substances when made by a particular process. It will presumably still be possible for claims to be made for improved processes of manufacture for substances which are already the subject of a product claim by an earlier inventor. 'Cross licensing' would then probably ensue. The provisions for Compulsory Licences which the Comptroller is empowered to grant are generally strengthened and should continue to ensure that no patent relating to a medicinal or food substance is used in a manner contrary to the public interest. The other changes which deserve mention are the additional powers accorded to the Comptroller and the extension of the grounds of opposition. The Comptroller is now empowered to direct that a reference be inserted in an applicant's complete specification to any other prior patent claims which he considers might be infringed by the performance of the applicant's invention. Additional grounds of opposition are 'prior user,' that the subject matter of any claim is obvious and clearly does not involve any inventive step, or that it is not an invention within the meaning of the Act. It may reasonably be hoped that these latter changes will combine to avert a number of trivial specifications which would otherwise constitute so much 'dead wood' in the industry, even if they had no more serious obstructive influence.

The proceedings arising from the Petition to the High Court by Boots Pure Drug Co. Ltd. for the revocation of Letters Patent No. 533,495 granted to May and Baker Ltd. and Ciba Ltd., more colloquially the 'Sulphathiazole Case,' constitute probably the most important chemical case for many years and have attracted considerable attention. The account of the proceedings merits careful study by chemists concerned in any way with chemotherapeutic patents. The masterly analysis given in the judgment[3] of Mr. Justice Jenkins is of great value. The judgment was upheld in the Court of Appeal; in the House of Lords the judgment was upheld by a majority decision, three of the judgments holding that the amendment was not allowable and two of the judgments being in dissent. J. G. Fife has recently discussed[4] some of the issues, but it

is appropriate to summarize them here. The patent in suit, 533,495, is a typical chemotherapeutic patent. Certain *p*-aminobenzenesulphonamidothiazoles were found to be far more active against experimental infections in mice than the then known sulphanilamide and accordingly patents were filed. Since purely substance claims were at that time not admissible, a manner of manufacture had to be claimed and this in fact amounted to all the foreseeable and obvious methods as applied to the new class of sulphonamidothiazoles. By itself this would not have constituted a valid invention, but valuable and unexpected therapeutic properties which conferred utility on the class would bring it within the interpretation of an invention. The complete specification contained the general statement that 'the new *para*-aminobenzene-sulphonamidothiazoles find application in therapeutics' and illustrated this by reference to results with sulphathiazole and sulphamethylthiazole compared with sulphanilamide against experimental infections in mice. Although these two sulphonamides were specifically mentioned in the body of the specification and were the subject of examples describing the manner of manufacture, they were not the subject of a specific claim as such. All the claims were broad, and in fact claimed *p*-aminobenzenesulphonamidothiazoles. Few chemists would have appreciated at first sight just how broad such a claim really was. It was admitted that the patent as it stood was invalid and in face of a petition for revocation by Boots the patentees, May and Baker and Ciba, sought to amend it by restricting it by way of disclaimer to the two sulphonamides exemplified. This amendment was opposed by Boots on various grounds, but basically because the amendment, if allowed, would make the invention substantially different from the original invention.

The final majority decision, which results in the revocation of the patent, is obviously of the utmost importance to the industry because a very large number of patents in this field are of the same general character and may well be invalid. The case illustrates the fundamental difficulty of the patentees in the field of medicinal substances. Rarely will it be possible, in the time available for completing a patent, to assess adequately the clinical value of new therapeutic substances and precisely to define the scope of the invention which produced them. The dilemma lies between too broad a claim, which later work might not entirely support and thus make the patent invalid, and too narrow a claim, which may enable competitors to operate just outside its scope and so deprive the patentee of the benefits which he is entitled to expect from his original invention. It is not apparent that the re-introduction of substance claims in the 1949 Act does anything to resolve this dilemma directly. But it may be hoped that it will gradually induce a trend away from efforts to protect all possible processes (whether economic or not) for new medicinal substances and thus enable more resources to be devoted to the discovery of further new and improved substances and the thorough investigation of their uses. Although this may mean that some interesting and ingenious syntheses may not be brought to light so soon, there is little doubt this possible loss would be more than outweighed by the greater gain on the other score. Evidently the effects of the new legislation will not be apparent until it has been in operation for some

considerable time and inevitably some interpretations will remain matters of opinion until court judgments become available. In the view of this Report the factors discussed will make for a healthier patent climate in the medicinal chemicals industry.

References

1 *Brit. med. J.*, 1949, ii, 434
2 Patents and Designs Acts, Reports of Departmental Committee, Cmd. 6618, 6789, 7106
3 65, R.P.C. 266
4 R.I.C. Lectures, Monographs & Reports, 1949, No. 5, 12

ANTIHISTAMINES (D. W. Adamson, M.Sc.(Tech.), Ph.D., D.Phil., A.R.I.C.)

The Wellcome Research Laboratories, Chemical Division

THE demonstration by Bovet[1] in 1937 that certain ethers had the property of antagonizing the action of histamine in animals, followed in 1942[2] by the successful use of histamine antagonists in certain allergic conditions in man, stimulated a great deal of research on the part of pharmaceutical firms. Many hundreds of compounds which have some antihistamine action are now known and the medical man, especially in the U.S.A., has the choice of a large (perhaps excessive) number of commercial drugs, many of which apparently differ little in therapeutic value.

The medical profession was quick to realize the potential value of histamine antagonists which have been tested in a large number and variety of human diseases. The position of the antihistamines in the treatment of certain allergic diseases, notably urticaria, hay-fever and rhinitis, is well established and there have been reports of beneficial effects in other conditions, some not obviously within the allergic group. More recent applications have included, for example, treatment of Parkinson's disease,[3] sea-sickness[4] and nausea and vomiting in pregnancy.[5] The early hope that the antihistamines would be of value in asthma was not fulfilled, although the more potent drugs are useful in mild attacks when treated at an early stage.[6]

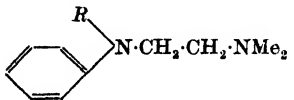
A report[7] that antihistamines were effective in alleviating the symptoms of the common cold aroused great interest and for some weeks the antihistamines enjoyed a prominent place in the popular press. The difficulty of assessing 'cold cures' has been emphasized[8] and full appraisal of the claims must await the results of large-scale controlled clinical trials. Meanwhile, the dangers of indiscriminate self-medication with antihistamines, none of which are entirely free from side-effects such as drowsiness or giddiness, have been pointed out.[9]

In the present report earlier work is summarized to provide a background to the review of progress made in the chemistry of the subject during 1949. The term 'antihistamine' has been adopted in preference to the alternative 'antihistaminic,' 'histamine antagonist' or 'histaminolytic.' References[10] are given to some published reviews.

Diamines

Of the great number of compounds investigated for antihistamine activity those either derived directly from ethylenediamine or which incorporate the carbon–nitrogen skeleton of ethylenediamine in their structure have been the most numerous. Until very recently all the most potent antihistamines have been found in this series.

(*a*) *Derivatives of ethylenediamine.*—Antergan [(I), *R* = $PhCH_2$], the first antihistamine to be used successfully in the treatment of allergic conditions in man, was introduced by Halpern[2] in 1942. The search for more effective compounds of this type culminated in the discovery of Neoantergan [(Anthisan, (II)] by Bovet[11] in 1944. Neoantergan is highly specific in its action and remains one of the most potent of the antihistamines; the preparation of this and related compounds is described in a series of patents.[12] Meanwhile, workers in U.S.A. were proceeding independently along similar lines, and in 1945[13] Pyribenzamine [Tripelennamine (III), *R* = $PhCH_2$), a compound closely related to Neoantergan with similar though somewhat lower activity, was introduced.



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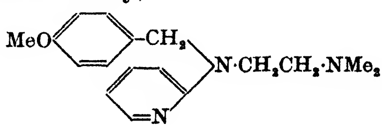

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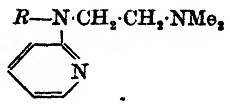


(III)

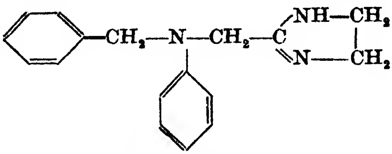
In recent years extensive surveys have revealed many potent anti histamines among analogues of Antergan and Neoantergan and several of these have been put on the market, e.g. Thenylene (Histadyl; III, *R* = 2-thienylmethyl)[14]; Chlorothen [Tagathen (III), *R* = 2-(5′-chloro)-thienylmethyl][15] and the corresponding bromo-compound, Bromothen[15]; Neohetramine[16] in which the α-pyridyl group of Neoantergan is replaced by 2-pyrimidyl; Diatrin [(I), *R* = 2-thienylmethyl].

Some relationships between activity and structure in this series have been discussed by Scholz[18] and Bovet.[10(g)] In the more active compounds, one amino group of ethylenediamine is replaced by dimethylamino and the other amino group is substituted by a phenyl or *N*-heterocyclyl group and by an aralkyl group. The highest activity is associated with the α-pyridyl group; drastic reduction in activity results if the pyridyl group is attached at the β- or γ-position, or if the α-pyridyl group carries methyl substituents. The aralkyl group may be benzyl, *para*-substituted benzyl, thenyl, substituted thenyl or furyl.

During 1949 this field was extended and many new compounds, some having the same order of potency as the earlier drugs, were described. Analogues of Thenylene in which the thienyl group is attached at the 3-position were effective antihistamines,[19] and Thenfadil [(III), *R* = 3′-thienylmethyl] was selected for detailed study.[20] Substitution of the

thienyl or the pyridyl group of Thenylene did not increase the potency above that of Chlorothen.[21] The introduction of *para*-fluoro or -chloro into the benzyl group of Pyribenzamine led to increased potency[22]; other variations in the aralkyl group have been described.[23] Replacement of the α-pyridyl group of Pyribenzamine by quinoxalyl[24] and by lepidyl[25] has been described; the 2-thiazolyl group in place of the α-pyridyl of Neoantergan gave an effective antihistamine.[26] The replacement of the dimethylamino group by pyrrolidino,[27] which enhanced activity in other series, led to diminished activity in this series. A quantitative method for the determination of antihistamine compounds containing the pyridine group has been developed and applied in following the course of Pyribenzamine in the body.[28]

One of the earlier antihistamines, Antistin (IV), introduced in Switzerland in 1946[29] may be regarded as related to Antergan, the 2-methyliminazoline group replacing the dimethylaminoethyl moiety.



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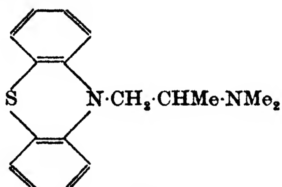
(*b*) *Phenothiazine derivatives.*—Phenergan [R.P. 3277 (V)], introduced by Halpern,[30] is particularly important on account of its prolonged action which allows its administration to be limited to a single daily dose.[31]



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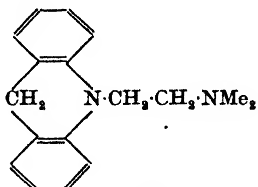

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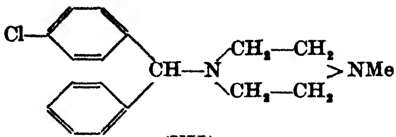
These compounds were synthesized by Charpentier[32] by reacting phenothiazine with the appropriate β-chloralkylamines in the presence of sodamide; Phenergan, originally formulated as a β-dimethylamino*iso*propyl derivative, has now been shown, by degradation studies,[33] to have the structure (V). High activity was retained when the dimethylamino group was replaced by pyrrolidino[34] (as in Pyrrolazote) but the diethylamino analogue had but feeble antihistamine activity. No advantage was gained by the introduction of methoxy substituents. Replacement of the S bridge by O, SO or SO_2 removed or drastically reduced activity; on the other hand, it has been stated in a preliminary report[35] that some acridans, e.g. (VI), in which the S bridge of phenothiazine is replaced by CH_2, have outstanding activity.

(*c*) *Cyclic diamines.*—A series of 1- and 1 : 4-substituted derivatives of piperazine were examined several years ago[36] and some were found

to have a moderate antihistamine activity. Recently a series of *N*-methylpiperazines was synthesized independently in two laboratories.[37,38] The most effective was 1-(4′-chlorbenzhydryl)-4-methylpiperazine [Histantin, Di-paralene (VII)] which has a persistent action and is relatively free from side-effects.

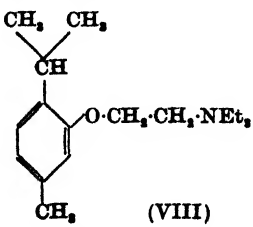


(VII)

Other diamines in which one of the nitrogen atoms is contained in a cyclic structure and which are structurally related to Antergan have been prepared as potential antihistamines, e.g. *N*-dimethylaminoethyl derivatives of substituted quinolines,[39] and of indole and carbazole derivatives[40]; derivatives of 4- and 3-aminopiperidine.[41]

Ethers

The discovery in 1937 by Bovet and his colleagues[1] at the Institut Pasteur that some others, e.g. 929F (VIII) antagonized histamine as well as adrenaline may be regarded as the starting point of modern antihistamine research. Benadryl [Diphenydramine (IX)],[42] the first ether to have clinical importance as an antihistamine, has become one of the best known and widely used antihistamines; its introduction in 1945 stimulated a great deal of valuable pharmacological and clinical research. A large number of isomers and analogues have been prepared by the original inventors[43] and by others, but none appears to offer any marked advantages over the parent compound. The dimethylamino group may be replaced by piperidino, morpholino[42] or pyrrolidino[44] without great change in activity, and the quaternary salts[45] retain some antihistamine action. Substitutions in the benzhydryl group in general led to major loss of activity, but the introduction of a methyl group appeared to have a favourable effect.[46,47] Some sulphur analogues of Benadryl have been



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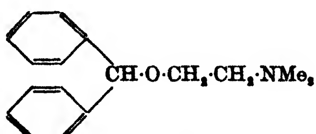

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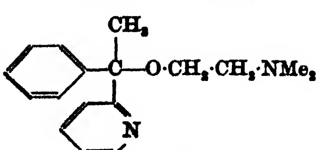

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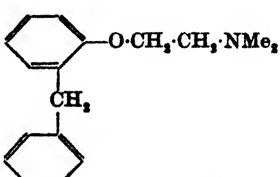


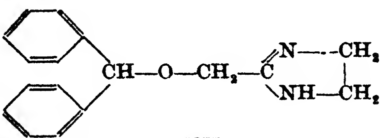
(XI)

prepared.[48] A number of basic ethers derived from pyridyl phenyl carbinols[49,50] have antihistamine activity, which is at a maximum in Decapryn (X). A series of aminoalkyl ethers from benzylphenols[51,52] included several very potent compounds, (XI) being among the most promising.

Benadryl, like most antihistamines, induces drowsiness and a feeling of fatigue and attempts to overcome this defect have been made by combining it with compounds which have a central stimulant action, e.g. Dramamine[53] is the stable salt formed from Benadryl base and 8-chlorotheophyllin. Dramamine, which is effective as an antihistamine *per se*,[4,5] is of value in the treatment of radiation sickness,[54] an effect which is probably due to some other cause than antagonism of histamine.[55]

The distribution and excretion of radioactive Benadryl, in which ^{14}C is incorporated in the molecule in the α-position of the benzhydryl group, has been studied.[56]

The activity of Antistin (IV) suggested the replacement of the dialkylaminoethyl moiety by the 2-methyliminazoline group in ethers such as 929F (VIII) to give a series of 2-aryloxymethyliminazolines.[57] These were weakly active, but the compound (XII) theoretically derived from Benadryl by the same change is a potent antihistamine.[58,59]

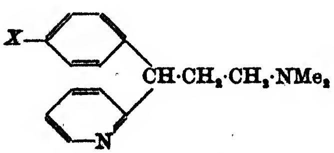


(XII)

Miscellaneous

A new group of antihistamines incorporating the carbon-nitrogen skeleton of *n*-propylamine has recently come into prominence. Trimeton [(XIII), $X = H$][60] was an effective antihistamine,[61] and it has been stated in a preliminary announcement[62] that the introduction of a *p*-chloro group [Chlor-Trimeton (XIII), $X = Cl$) increased activity to a very high level. This series is related to the $\gamma:\gamma$-diphenylpropylamine (XIV) which has a weak antihistamine action and was used several years ago in the treatment of asthma.[63]

Thephorin [Phenindamine (XV)][64] provides an example of an entirely new structure in the antihistamine field and some interesting chemical reactions are involved in its synthesis from bis(benzoylethyl)methylamine.[65] It may be noted that the $\gamma:\gamma$-diphenylpropylamino moiety may be traced in its structure.



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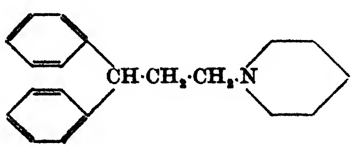
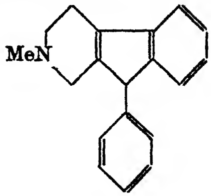
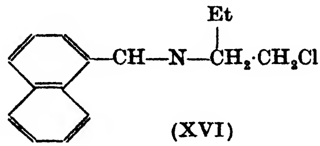


(XIV)



(XV)

The discovery that some compounds, e.g. (XVI), which are powerful adrenergic blocking agents also are very potent antihistamines (comparable to Neoantergan in activity) is of considerable biological interest.[66]



(XVI)

In view of the generally accepted hypothesis that antihistamines act by competitive antagonism, it is surprising that compounds with a close structural resemblance to histamine have been neglected until recently; during 1949 aminomethyliminazoles,[67] triazoles[68] and some benziminazole derivatives[69] have been examined. Compounds which have been synthesized in an attempt to correlate structure with histamine-like activity[70] come into the same category. So far no compound with any appreciable antihistamine action has emerged from these studies.

References

1 Ungar, Parrot and Bovet, *C.R. Soc. Biol., Paris*, 1937, **124**, 445; Staub and Bovet, ibid., 547
2 Halpern, *Arch. int. Pharmacodyn.*, 1942, **68**, 339
3 Ryan and Wood, *Lancet*, 1949, i, 258
4 Gay and Carliner, *Science*, 1949, **109**, 359
5 Carliner, Radman and Gay, ibid., 1949, **110**, 215; Dongray, *Brit. med. J.*, **1949**, 1081
6 Herxheimer, *Brit. med. J.*, **1949**, 901
7 Brewster, *U.S. Naval med. Bull.*, 1949, **49**, 1
8 Paton, Fulton and Andrewes, *Lancet*, 1949, i, 935
9 Editorial, ibid., 1950, i, 28
10 Reviews: (a) Bovet and Walthert, *Ann. pharm. franç.*, 1944, **2**, 3; (b) Feinberg, *J. Amer. med. Ass.*, 1946, **132**, 702; (c) Viaud, *Prod. Pharm.*, 1947, **2**, 53; (d) Loew, *Physiol. Rev.*, 1947, **27**, 542; (e) Huttrer, *Enzymologia*, Amsterdam, 1948, **12**, 277; (f) Hunter and Dunlop, *Quart. J. Med.*, 1948, **17**, 271; (g) Bovet and Bovet-Nitti, 'Structure et Activité Pharmacodynamique des Medicaments du Système Nerveux,' 1948 (Bâles Karger)
11 Bovet, Horclois and Walthert, *C.R. Soc. Biol., Paris*, 1944, **138**, 99
12 B.P. 594,603; 604,675; 604,678–80; 606,181–2; 606,187
13 Mayer, Huttrer and Scholz, *Science*, 1945, **102**, 93;
Huttrer, Djerassi, Beears, Mayer and Scholz, *J. Amer. chem. Soc.*, 1946, **68**, 1999; U.S.P. 2,406,594
14 Weston, *J. Amer. chem. Soc.*, 1947, **69**, 980; Lee, Dinwiddie and Chen, *J. Pharm. exp. Ther.*, 1947, **90**, 83
15 Clapp, Clark, Vaughan, English and Anderson, *J. Amer. chem. Soc.*, 1947, **69**, 1549; Litchfield, Adams, Goddard, Jaeger and Alonso, *Bull. Johns. Hopk. Hosp.*, 1947, **81**, 55

[16] Reinhard and Scuci, *Proc. Soc. exp. Biol. Med.*, 1947, **66**, 512; Dreyer and Harwood, ibid., 515
[17] Ercoli, Schacter, Hueper and Lewis, *J. Pharm. exp. Ther.*, 1948, **93**, 210
[18] Scholz, 1st National Symposium for Medicinal Chemistry, Ann Arbor, 1948
[19] Campaigne and Le Suer, *J. Amer. chem. Soc.*, 1949, **71**, 333
[20] Hoppe and Lands, *J. Pharm. exp. Ther.*, 1949, **97**, 371
[21] Clark, Clapp, Vaughan, Sutherland, Winterbottom, Anderson, Forsythe, Blodinger, Eberlin and English, *J. org. Chem.*, 1949, **14**, 216
[22] Vaughan, Anderson, Clapp, Clark, English, Howard, Marson, Sutherland and Denton, ibid., 228
[23] Biel, *J. Amer. chem. Soc.*, 1949, **71**, 1306
[24] Gardner and Stevens, ibid., 1868
[25] Kaye, ibid., 2322
[26] Bernstein and Feinberg, *J. Lab. clin. Med.*, 1949, **34**, 1007
[27] Lincoln, Heinzelmann and Hunter, *J. Amer. chem. Soc.*, 1949, **71**, 2902
[28] Perlman, *J. Pharm exp. Ther.*, 1949, **95**. 465
[29] Meier and Bucher, *Schweiz. med. woch.*, 1946, **76**, 294
[30] Halpern and Ducrot, *C.R. Soc. Biol., Paris*, 1946, **140**, 361
[31] Bain, Broadbent and Warin, *Lancet*, 1949, ii, 47
[32] B.P. 608,208
[33] Charpentier, *C.R. Acad. Sci., Paris*, 1947, **225**, 306
[34] Reid, Wright, Kolloff and Hunter, *J. Amer. chem. Soc.*, 1948, **70**, 3100
[35] Freese, Hambourger and Michiels, *Fed. Proc.*, 1948, **7**, 219
[36] Cerkovnikov and Stern, *Brit. Abs.*, 1948 [AII], 129
[37] Hamlin, Weston, Fischer and Michaels, *J. Amer. chem. Soc.*, 1949, **71**, 2731
[38] Baltzly, DuBreuil, Ide and Lorz, *J. org. Chem.*, 1949, **14**, 775; Castillo, de Beer and Jaros, *J. Pharm. exp. Ther.*, 1949, **96**, 388
[39] Carara, D'Amato and Pagani, *Chem. Abs.*, 1948, **42**, 6988
[40] Wright, *J. Amer. chem. Soc.*, 1949, **71**, 1028
[41] Reitsema and Hunter, ibid., 1948, **70**, 4009; 1949, **71**, 1680
[42] Loew, Kaiser and Moore, *J. Pharm. exp. Ther.*, 1945, **83**, 120; Rieveschl, U.S.P. 2,421,714
[43] B.P. 605,915–6; 606,158; 606,317; 607, 258; U.S.P. 2,427,878; 2,455,949
[44] Wright, Kolloff and Hunter, *J. Amer. chem. Soc.*, 1948, **70**, 3098
[45] Winder, Kaiser, Anderson and Glassco, *J. Pharm. exp. Ther.*, 1946, **87**, 121
[46] Schulman and Fuchs, *Ann. Allergy*, 1949, **7**, 502
[47] Protiva and Borovicka, *Brit. Abs.*, 1949 [AII], 500
[48] Protiva, Jilek, Kolinsky, Rericha and Urban, ibid., 666
[49] Tilford, Shelton and Van Campen, *J. Amer. chem. Soc.*, 1948, **70**, 4001; ibid., 1949, **71**, 1885
[50] Sperber, Papa, Schwenk and Sherlock, ibid., 1949, **71**, 887
[51] Cheney, Smith and Binkley, ibid., 60
[52] Wheatley, Cheney and Binkley, ibid., 64, 3795
[53] Cusic, *Science*, 1949, **109**, 574
[54] Beeler, Tillisch and Popp, *Proc. Mayo Clin.*, 1949, **24**, 477
[55] Annotation, *Lancet*, 1949, ii, 999
[56] Glazko, McGinty, Dill, Wilson and Ward, *J. biol. Chem.*, 1949, **179**, 409
[57] Djerassi and Scholz, *J. Amer. chem. Soc.*, 1947, **69**, 1688
[58] Dahlborn and Sjögren, *Acta chem. scand.*, 1947, **1**, 777; 1949, **3**, 32
[59] Djerassi and Scholz, *J. org. Chem.*, 1948, **13**, 830
[60] Sperber, Papa, Schwenk, Sherlock and Fricano, Abs. 1948 Chicago Meeting, Amer. Chem. Soc., p. 4K; B.P. Appl. 25,947, 26,873, 27,020/48
[61] La Belle and Tislow, *Fed. Proc.*, 1948, **7**, 236
[62] Tislow, La Belle, Makorsky, Reed, Cunningham, Emele, Grandage and Roggenhofer, ibid., 1949, **8**, 338
[63] Schaumann, *Med. u. Chem.*, 1943, **4**, 229
[64] Lehmann, *J. Pharm. exp. Ther.*, 1948, **92**, 249
[65] Plati and Wenner, *J. org. Chem.*, 1949, **14**, 543; U.S.P. 2,470,108–9
[66] Achenbach and Loew, *Fed. Proc.*, 1947, **6**, 304
[67] Turner, Ruebner and Scholz, *J. Amer. chem. Soc.*, 1949, **71**, 2801
[68] Sheehan and Robinson, ibid., 1436
[69] Wright, ibid., 2035
[70] Lee and Jones, *J. Pharm. exp. Ther.*, 1949, **95**, 71

STEROID CHEMISTRY (V. Petrow, D.Sc., A.R.I.C. and G. E. H. Skrimshire, F.R.I.C.)

The British Drug Houses Ltd.

General

THE ability of cholesterol to form complexes has been utilized in two recent patents[1,2] dealing with its isolation from natural sources. These describe addition products of cholesterol with metal nitrates such as aluminium nitrate and with succinic acid which, on treatment with water, are decomposed to yield the free sterol. The succinic acid process is claimed to give better yields than the well known method using oxalic acid.

The direct formation of products with antirachitic activity from steroid materials by treatment with acetic anhydride and sulphuric acid[3] has been further investigated by Yoder and Thomas.[4,5] These authors, believing 'antirachitic sulphonation' to be an oxidizing reaction, have prepared and sulphonated a number of oxidized derivatives of cholesterol, including cholestan-3β : 5α : 6β-triol, 3 : 6-diacetoxy-5-methyl-10-norcholest-8(9)-ene ('diacetate of Westphalen's diol') and cholest-5-ene-3β : 4β-diol. All the sulphonated products had high antirachitic potency as measured by the healing response of rachitic rats, although the feeding was accompanied by loss in weight. Unsulphonated 3 : 6-diacetoxy-5-methyl-10-norcholest-8(9)-ene was inactive.

Direct sulphonation of crude cholesterol-containing materials such as the unsaponifiable fraction of wool fat also yields products of considerable antirachitic potency[5] as judged by the increase in percentage bone-ash in the tibiæ of young chicks. When fed at low levels, the sulphonated product appears to be more effective in preventing rickets than a reference cod-liver oil fed in comparable amounts, but the difference is not maintained when larger doses are given. Similarly, the increases in live weight of the chicks following the feeding of the sulphonated sterol is greater than with cod-liver oil when the comparison is made at low feeding levels. The antirachitic substance produced by the sulphonation process must necessarily differ from the vitamin *D* present in cod-liver oil since sulphonation of the latter destroys its vitamin *D* activity. These very interesting results may well lead to a technical utilization of unsaponifiable fractions containing sterols.

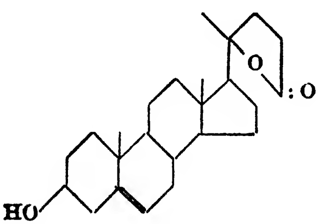
7-*Dehydrocholesterol* (*Provitamin* D_3).—In a paper on 'α'-spinasterol,[6] Fieser, Fieser and Chakravarti describe improvements in the Windaus method for the preparation of 7-dehydrocholesterol. Yields have been increased by conducting the oxidation to the 7-ketone under anhydrous conditions and effecting reduction of the 7-carbonyl group with lithium aluminium hydride.

Bernstein *et al.*[7] have investigated the *N*-bromosuccinimide bromination of cholesteryl esters and dehydrobromination of the resulting 7-bromo compounds to 7-dehydrocholesterol. They claim that consistently high yields are obtained by their procedure.

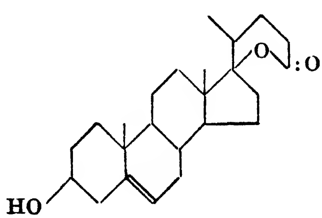
Bromination with *N*-bromosuccinimide in the 'allylic position'[8] has proved valuable in the field of steroid chemistry and has already made many useful intermediates available for the first time. Considerable interest will therefore be shown in a recent communication[9] which states that cholesteryl esters can be brominated directly in the 'allylic position' by bromine in carbon tetrachloride in the presence of light of wavelength 4100Å. Bromination is said to take place almost exclusively in position 7 to give a 7-bromocholesteryl ester in 55–65% yield.

In addition to its use as a brominating agent, *N*-bromosuccinimide has acquired added technical importance as a selective oxidant of the 7-hydroxyl group of cholic acid.[10] The oxidation is carried out in sodium bicarbonate solution and the total product reduced by the Wolff–Kishner process as modified by Huang-Minlon, desoxycholic acid being isolated as the etherate in a yield of 68%. Desoxycholic acid itself is totally unaffected by *N*-bromosuccinimide and it is therefore possible to use the total acids from the bile hydrolysate for the oxidation, the product being reduced and processed as before. Lithocholic acid and other contaminants are removed at the etherate stage.

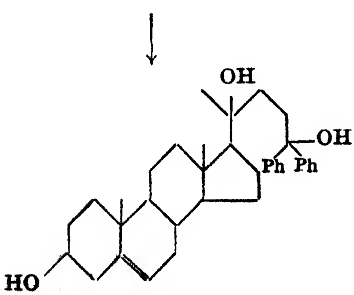
Lactonic oxidation product of cholesteryl acetate dibromide.—The lactone isolated from the neutral products of oxidation of cholesteryl acetate dibromide with chromic acid[11] and believed by Billeter and Miescher[12] to be 3β-20-dihydroxy-chol-5-enic-24 : 20-lactone (I) has now been shown by the same authors[13] to be 3β : 17-dihydroxy-chol-5-enic-24 : 17-lactone (IV). Billeter and Miescher were led to adopt the 24 : 40 structure (I) following the observation that a Grignard reaction with phenyl magnesium bromide gave a diol (II), dehydrated to a diene (III) which could be oxidized to pregnenolone.



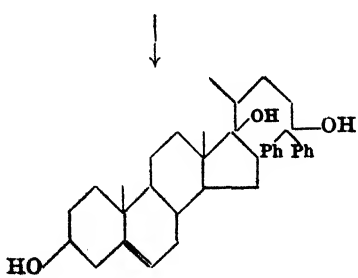
(I)



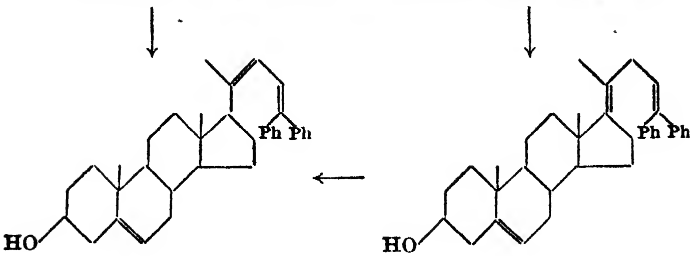
(IV)



(II)



(V)



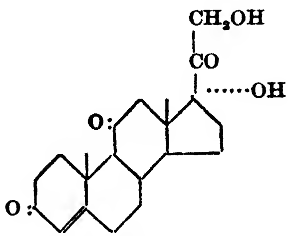
(III) (VI)

The 24 : 17 lactone structure (IV) was not excluded by this evidence however, since the 17(20) double bond in the diene (VI) could conceivably move to position 20(22) where it would be in conjugation with the other double bond and the two benzene nuclei. Billeter and Miescher have now demonstrated[12] by synthetic methods that the lactone must have the 24 : 17 structure, and that the rearrangement of diene (VI) to diene (III) does occur.

It is interesting to recall in connexion with this work that Veer and Goldschmidt[14] actually obtained a very small yield of dehydro*epi*-androsterone by the energetic oxidation of the triol 3-monoacetate obtained by Grignard reaction on the lactone. These authors accordingly assigned it a structure showing a lactone link at C-17, but underestimated the length of the chain, describing the compound as the lactone of 3β : 17-dihydroxynorchol-5-enic acid.

Cortisone (Compound E)

The most important work in the steroid field during 1949 has undoubtedly been that in relation to Cortisone (Kendall's Compound E).



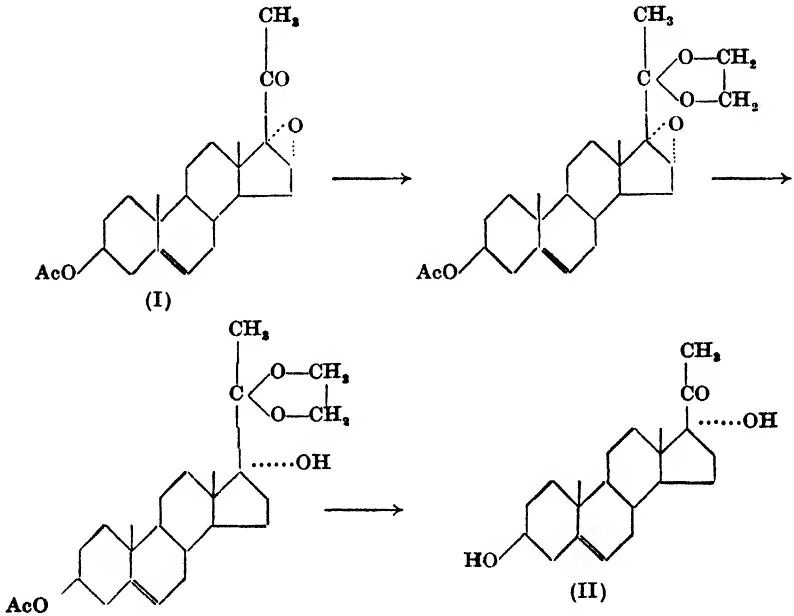
Cortisone

The reported clinical value of this corticosteroid in rheumatoid arthritis has stimulated research on methods of synthesis of Cortisone itself and substances related to it. Recently, the emphasis has been mainly of the introduction of the α-orientated hydroxyl group at position 17 and synthesis of the 17-ketol side-chain.

The reduction of 16 : 17-epoxides to 17α-hydroxy compounds has been the subject of several papers. Plattner, Heusser and Feurer,[15] using lithium aluminium hydride, reduced the 16 : 17-epoxides derived from 3β-acetoxy-5-*allo*pregn-16-en-20-one and obtained 40% of Reichstein's

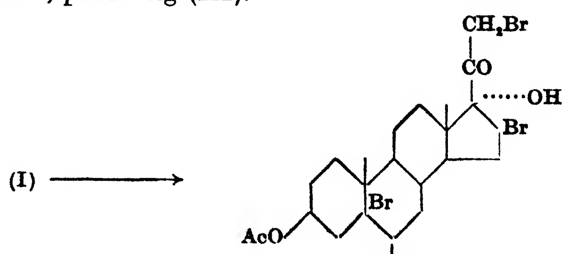
Substance J (5-*allo*pregnan-3β : 17α : 20β-triol) and 20% of Substance O, the 20-epimer of J.

Julian, Meyer and Ryden[16] likewise prepared Substances J and O, and also applied the method to the reduction of 16 : 17-epoxypregn-5-en-3β-ol-20-one (I). The keto group in position 20 was protected by the formation of a cyclic ketal, the product, after reduction, being hydrolysed to give pregn-5-en-3β : 17α-diol-20-one (II).



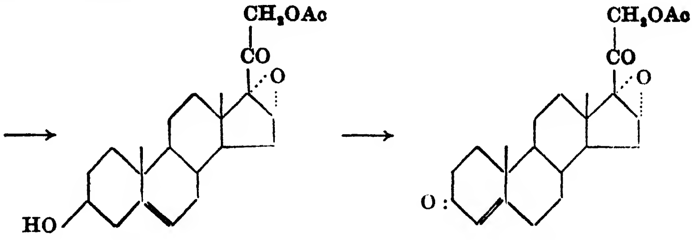
Again, using 16 : 17-epoxypregn-5-en-3β-ol-20-one as starting material, Julian and co-workers[17] have prepared 17α-hydroxyprogesterone and 17α-hydroxy-11-desoxycorticosterone acetate [acetate of Reichstein's Compound S (VI)] by the following method.

The 16 : 17-epoxy compound (I) is treated successively with one molecular equivalent of bromine in acetic acid/carbon tetrachloride, then with hydrogen bromide in acetic acid, followed by a second molecular equivalent of bromine, producing (III).

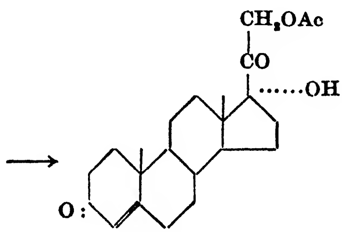


(III)

Hydrolysis of (III) with hydrogen bromide in methanol/benzene, followed by treatment with sodium iodide in benzene/ethanol and finally with potassium acetate in acetone, yields (IV), which on Oppenauer oxidation gives (V).



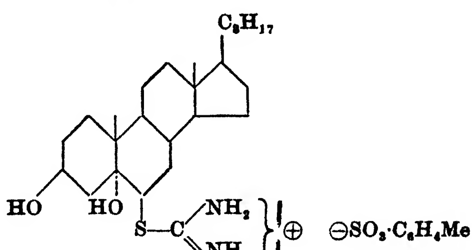
(IV) (V)



(VI)

Hydrolysis with hydrogen bromide in acetic acid, followed by reduction with Raney nickel, yields (VI).

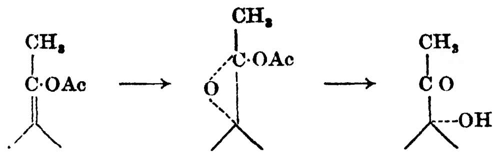
Recently, yet another method for the reduction of the steroid oxides has been published by King and Campbell.[18] α-Cholesteryl oxide has been found to react with thiourea and *p*-toluenesulphonic acid to give cholestan-3β : 5α-diol-6-*iso*-thiouronium tosylate (VII) in 73–92% yield. On shaking the latter in alcoholic solution with Raney nickel and sodium hydroxide, reduction occurs giving cholestan-3β : 5α-diol.



(VII)

The application of this method to the preparation of 17α-hydroxy steroids from the corresponding 16 : 17 or 17 : 20-epoxy compounds is stated to be in progress.

17α-Hydroxy-steroids have also been prepared[19] by the action of perbenzoic acid on a 20-enol acetate in benzene or chloroform solution, followed by the hydrolysis of the product. Pregnan-3α : 17α-diol-20-one (IX) has been obtained in this way from the enol-acetate of 3-acetoxy-pregnan-20-one (VIII).

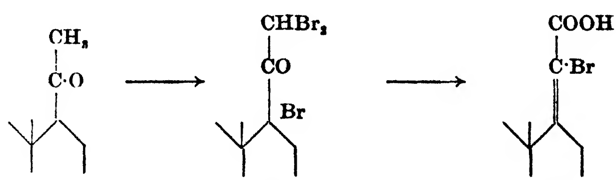


(VIII) (IX)

Its oxidation with *N*-bromoacetamide yields pregnan-17α-ol-3 : 20-dione from which the Δ^4-unsaturated ketone may be obtained by bromination and dehydrobromination. The process has also been applied to 11 : 20-diketosteroids, Koechlin *et al.*[20] obtaining pregnan-3α : 17α-diol-11 : 20-dione from the enol acetate of pregnan-3α-ol-11 : 20-dione.

Sarett[21] has reported an improvement to his earlier process[22] for the preparation of 21-acetoxypregnan-17α-ol-3 : 11 : 20-trione, a chemical precursor of Cortisone. The original method used pregnan-3α : 21-diol-11 : 20-dione 21-acetate as starting material and proceeded *via* the 20-cyanohydrin, the 3-keto-20-cyanohydrin, the 3-keto unsaturated nitrile and the 3-keto-20-cyano-17 : 20-osmate. The dehydration step, however, gave a poor yield owing to the adverse effect of the 3-keto grouping. In the improved method pregn-17-en-3α : 21-diol-20-cyano-11-one is partially acetylated to the 21-monoacetate which is then converted into the osmate ester with osmic acid. The osmate is sufficiently stable to chromic acid to permit oxidation of the 3-hydroxyl grouping to a 3-keto grouping. Hydrolysis of the osmate then yields the desired 21-acetoxy-pregnan-17α-ol-3 : 11 : 20-trione.

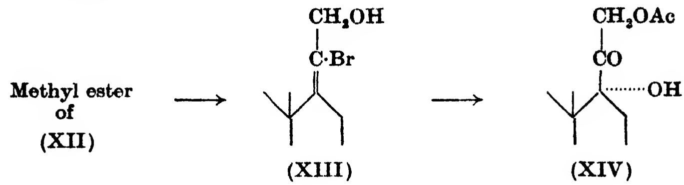
The most recent method of introducing the 17α-hydroxy group is due to Wagner and Moore[23] who employ the readily available bromopregnanolones. Thus 3β-acetoxy-17 : 21 : 21-tribromo-pregnan-20-one (XI), obtained by bromination of 3β-acetoxypregnan-20-one with three moles of bromine, is rearranged by treatment with alcoholic potassium hydroxide to pregn-17-en-3β-ol-20-bromo-21-oic acid (XII).



(X) (XI) (XII)

Reduction of the methyl ester of (XII) with lithium aluminium hydride gives the unsaturated 20-bromo-21-ol (XIII), the diacetate of which yields

pregnan-3β : 17α : 21-triol-20-one diacetate (XIV) on treatment with osmium tetroxide in ether.



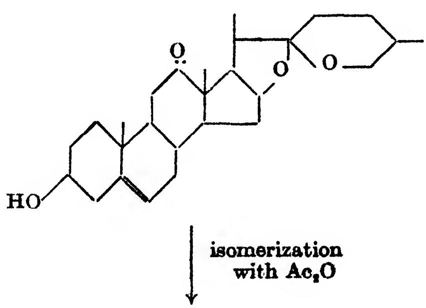
Introduction of the 21-hydroxyl grouping into pregnan-17α-ol-20-ones has been achieved by bromination and controlled hydrolysis.[20] Thus bromination of 3α-acetoxy-17α-hydroxy*allo*pregnan-20-one with one molar proportion of bromine yields the 21-bromo derivative. Hydrolysis of the latter is achieved employing 0·05N-sodium hydroxide in 60% ethanol at room temperature in a nitrogen atmosphere for 10 minutes, when replacement of the halogen by hydroxyl occurs. Acetylation then yields the diacetate of Reichstein's Compound P.

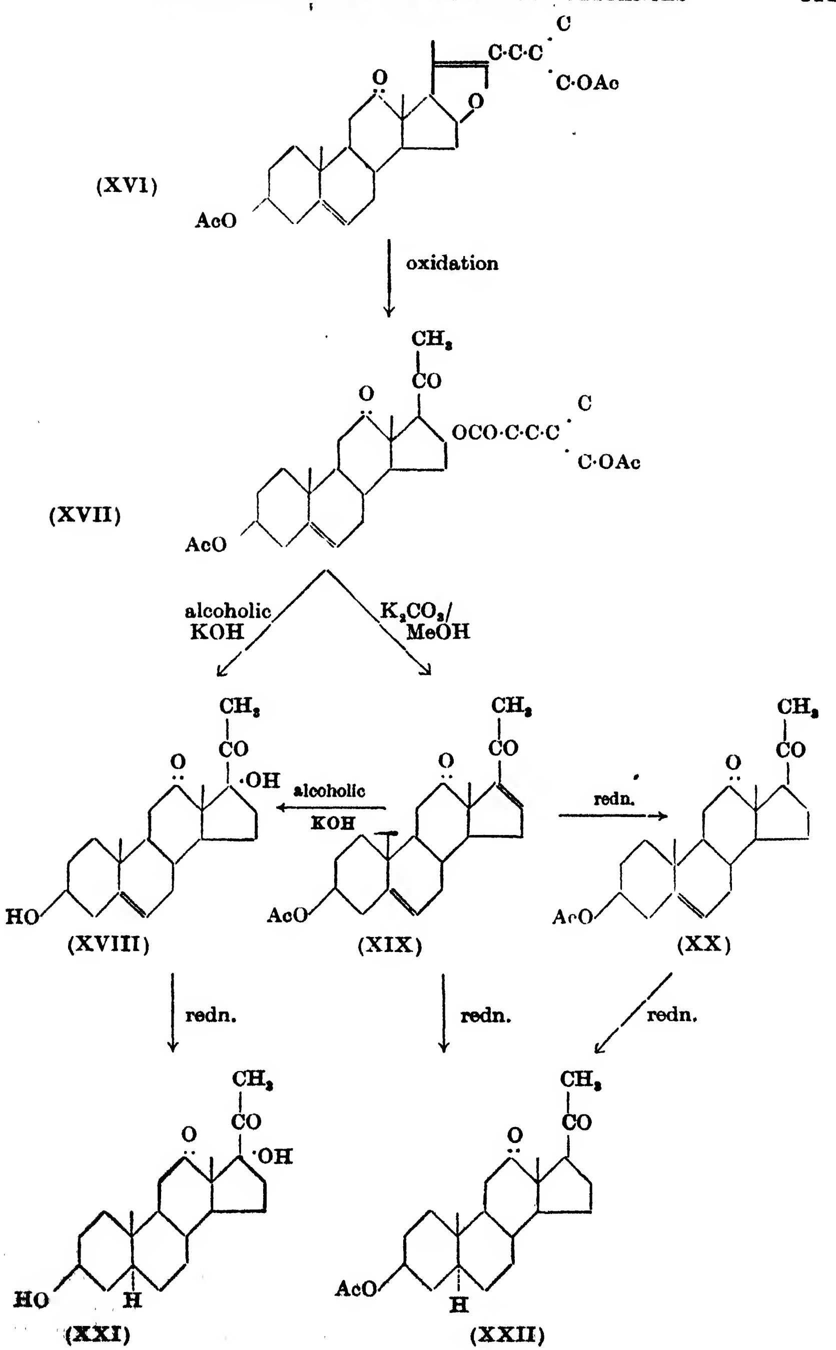
A variation of this method is used to prepare Reichstein's Compound S. In this case 3α-formoxy-17α-hydroxypregnan-20-one is converted into the 21-bromo derivative and the formoxy group hydrolysed off with dry hydrogen chloride and methanol at 5° C. for 5 hours. Oxidation with *N*-bromoacetamide yields 17α-hydroxy-21-bromopregnan-3 : 20-dione, which is hydrolysed by the procedure described to give, after acetylation, 21-acetoxy-17α-hydroxypregnan-3 : 20-dione. Bromination at position 4, followed by dehydrobromination then yields the acetate of Reichstein's Compound S.

Desoxycholic acid prepared from bile has hitherto been the main raw material for the production of Cortisone. It has been apparent for some time, however, that should Cortisone pass into clinical practice the supplies of bile available would become inadequate. Two naturally occurring genins, botogenin and sarmentogenin, have therefore been proposed as alternative starting materials.

Botogenin, a sapogenin obtained from *Dioscorea mexicana* was assigned structure (XV) by Marker,[24] who claimed[25] that it was easily degraded by the usual methods to pregn-5-en-3-ol-12 : 20-dione (XX).

(XV)




(XVI)
AcO
C·C·C
C
C·OAc
oxidation
(XVII)
CH$_3$
CO
OCO·C·C·C
alcoholic KOH
K_2CO_3/ MeOH
·OH
alcoholic KOH
redn.
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(XVIII)
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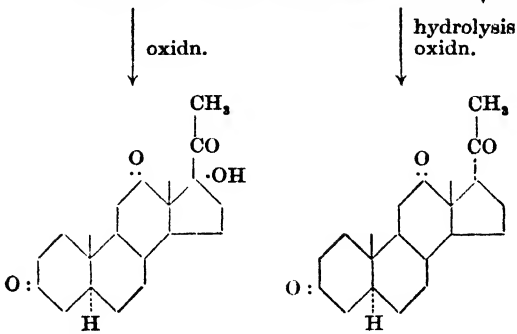
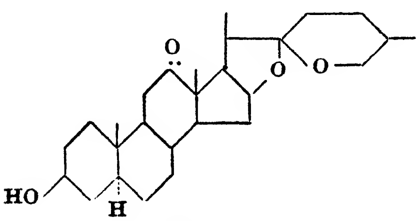
(XXI)
(XXII)



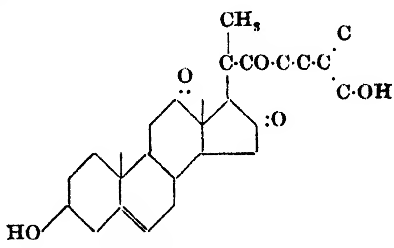
(XXIII) (XXIV)

Such a process was clearly shorter and simpler than the bromosuccinimide degradation of the bile-acid side-chain. In addition (XV) already had the necessary 5 : 6-unsaturated linkage. Reduction of (XX), followed by mild oxidation, gave a compound $C_{21}H_{30}O_4$ previously obtained by the oxidation of the related *pseudo*hecogenin and formulated as '*allo*pregnan-3 : 12 : 20-trione (XXIV) hydrate.'

A subsequent paper by Wagner, Moore and Forker,[26] however, threw doubt on the degradative evidence upon which Marker based structure (XV) for botogenin. Wagner *et al.* prepared what appeared to be authentic *allo*pregnan-3 : 12 : 20-trione from desoxycholic acid. This compound, in contrast to Marker's '*allo*pregnan-3 : 12 : 20-trione hydrate,' separated in the anhydrous form and was, moreover, quite different from its alleged 'hydrate.' The structural formulae of botogenin, hecogenin (XXV) and the related ricogenin, isolated by Marker[27] from *Dioscorea macrostachya* and assigned structure (XXVI) on the basis of its conversion to botogenin, thus appeared to require revision.



(XXV)



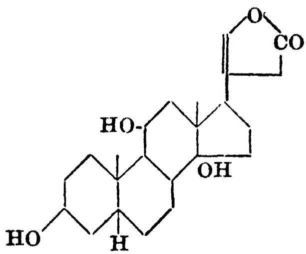
(XXVI)

The position has now been clarified by Marker,[28] who states that the '*allo*pregnan-3 : 12 : 20-trione hydrate' prepared by him from botogenin is in reality a 17-hydroxy*allo*pregnan-3 : 12 : 20-trione (XXIII) derived from 16-dehydropregn-5-en-3-ol-12 : 20-dione (XIX) by addition of the elements of water under the influence of strong alkali. Thus when hydrolysis of (XVII) is carried out with dilute methanolic potassium carbonate, immediate precipitation of the acetate of 16-dehydropregn-5-en-3-ol-12 : 20-dione (XIX) occurs which is thus removed from the

effects of further reaction. Alcoholic potassium hydroxide, on the other hand, gives (XVIII) directly from (XVII) or *via* (XIX).

As Marker points out, this is an extremely simple process for the production of 17-hydroxy compounds for the manufacture of Cortisone. It should be borne in mind, however, that there is as yet no evidence to show that the 17-hydroxy group so introduced has the necessary natural (α) configuration.

The formula for sarmentogenin, the cardiac aglycone derived from a species of *Strophanthus*, rests on a firmer experimental foundation. There seems little doubt that the compound is the 11-hydroxy steroid (XXVII).



(XXVII)

The seeds which yielded sarmentogenin were originally believed to come from *S. sarmentosus* but recent investigations by von Euw, Katz, Schmutz, and Reichstein[29] would indicate that some other, unidentified, species is involved. After preliminary study at the Royal Botanical Gardens, Kew, two members of this group of workers went to West Africa and collected samples of the seeds of *S. sarmentosus*. On examination the seeds were found to contain sarmentoside A, sarverside (a new substance) and only small quantities of sarmentogenin.

Whatever the origin of sarmentogenin it is obviously an excellent raw material for the preparation of Cortisone since it possesses an hydroxyl group at position 11, thus shortening the process by a considerable number of stages. The unsaturated lactone group also lends itself to a convenient transformation into a ketol of the corticosterone type.[30] Nevertheless, even when the actual species of *Strophanthus* is established the collection or cultivation of the necessary quantities of seeds will still be a formidable problem, and some years must elapse before adequate quantites of material can be forthcoming from this source.

A Swiss patent[31] describes the degradation of the aglycone digoxigenin into 3 : 11-dihydroetiocholanic acid, an attractive intermediate for the partial synthesis of Cortisone. The value of this claim appears doubtful, however, following the work of Mason and Hoehn,[32] which establishes digoxigenin as a 12-hydroxy compound.

References

1 B.P. 607,309; *Chem. Abs.*, 1949, **43**, 1158
2 B.P. 613,778; *Chem. Abs.*, 1949, **43**, 4433
3 Yoder, L., *J. biol. Chem.*, 1936, **116**, 71; Eck, J. C., Thomas, B. H. and Yoder, L., ibid., 1937, **117**, 655; Eck, J. C., and Thomas, B. H., ibid., 1937, **119**, 631; idem, ibid., 1939, **128**, 257

[4] Yoder, L. and Thomas, B. H., *J. biol. Chem.*, 1949, **178**, 363
[5] Idem, *Ind. Eng. Chem.*, 1949, **41**, 2286
[6] Fieser, L. F., Fieser, M. and Chakravarti, R. N., *J. Amer. chem. Soc.*, 1949, **71**, 2226
[7] Bernstein, S., Binovi, L. J., Dorfman, L., Sax, K. J. and Subbarow, T., *J. org. Chem.*, 1949, **14**, 433
[8] Ziegler, K., Späth, A., Schaaf, E., Schumann, W. and Winkelmann, E., *Ann. Chem.*, 1942, **551**, 80
[9] Schaltegger, H., *Experientia*, 1949, **5**, 321
[10] Fieser, L. F. and Rajogopalan, S., *J. Amer. chem. Soc.*, 1949, **71**, 3935
[11] Miescher, K. and Fischer, W. H., *Helv. chim. Acta*, 1939, **22**, 155.
[12] Billeter, J. R. and Miescher, K., ibid., 1947, **30**, 1409
[13] Idem, ibid., 1949, **32**, 564
[14] Veer, W. L. C. and St. Goldschmidt, *Rec. Trav. chim. Pays-Bas*, 1947, **66**, 75
[15] Plattner, P. A., Heusser, H. and Feurer, M., *Helv. chim. Acta*, 1948, **31**, 2210
[16] Julian, P. L., Meyer, E. W. and Ryden, I., *J. Amer. chem. Soc.*, 1949, **71**, 756
[17] Julian, P. L., Meyer, E. W., Karpel, W. J. and Ryden, I., ibid., 3574
[18] King, L. C. and Campbell, J. A., ibid., 3556
[19] Kritchevsky, T. H. and Gallagher, T. F., *J. biol. Chem.*, 1949, **179**, 507
[20] Koechlin, B. A., Garmaise, D. L., Kritchevsky, T. H. and Gallagher, T. F., *J. Amer. chem. Soc.*, 1949, **71**, 3262
[21] Sarett, L. H., ibid., 2443
[22] Idem, ibid., 1948, **70**, 1454
[23] Wagner, R. B. and Moore, J. A., ibid., 1949, **71**, 4160
[24] Marker, R. E. and Lopez, J., ibid., 1947, **69**, 2397
[25] Marker, R. E., ibid., 1949, **71**, 2656
[26] Wagner, R. B., Moore, J. A. and Forker, R. F., ibid., 3856
[27] Marker, R. E., ibid., 3856
[28] Idem, ibid., 4149
[29] von Euw, J., Katz, A., Schmutz, J. and Reichstein, T., 'Festschrift Prof. Paul Casparis,' p. 178, Pharm. Anstalt Univ. Basle
[30] Meyer, K. and Reichstein, T., *Helv. chim. Acta*, 1947, **30**, 1508
[31] Swiss Pat. 225,154; *Chem. Abs.*, 1949, **43**, 2244
[32] Mason, H. L., and Hoehn, W. M., *J. Amer. chem. Soc.*, 1938, **60**, 3034

AMINO-ACIDS AND POLYPEPTIDES (B. A. Hems, Ph.D., F.R.I.C.)

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General methods.—One or two investigations on general reactions of amino-acids require mention. P. Karrer *et al.* have applied lithium aluminium hydride to the esters of α-amino-acids to obtain the corresponding amino-alcohols. Reduction was carried out in the usual way with the amino-acid ester in ether. Yields are good and, when optically active esters are used, optically active amino-alcohols are obtained. In the first papers alcohols were prepared from L-alanine, L-leucine, L-proline, L-asparagine, DL-serine and L- and DL-phenylalanine esters,[1] and from

L-glutamic acid ester.[2] Similarly, L-tryptophanol,[3] L-valinol and L-tyrosinol[4] and L-histidinol[5] were prepared. In the last instance the ester of the dibenzoyl amino-acid was reduced, the free amino-alcohol being obtained after hydrolysis.

Mention has previously been made in ANNUAL REPORTS (1948, **33**, 587) of the resolution of amino-acids by the selective formation of an insoluble L-anilide when an acyl derivative of the amino-acid, aniline and papain are incubated together. A similar, but simpler, method has now been applied to methionine and tryptophan by M. Brenner *et al.*,[6] in which esters of the DL-acids are incubated together with a pancreatic enzyme preparation. The L-ester is selectively hydrolysed and the L-amino-acid separates out from the digestion mixture. The reaction is carried out in very concentrated mixtures of the esters and the yields of the optically active components are high (80–90%). Another method of resolution, also depending upon the stereo-selective action of enzymes, is described by V. E. Price, J. B. Gilbert and J. P. Greenstein,[7] in which *N*-acyl-DL-amino-acids are treated with a kidney or pancreas enzyme. This hydrolyses the L-derivative selectively, enabling simple separation of the L-amino-acid from the D-acylamino-acid to be achieved. The method has been applied to several amino-acids, including methionine, threonine, phenylalanine, tyrosine and tryptophan.

The application of synthetic resins to the isolation and separation of amino-acids is well known and has been extended by J. C. Winters and R. Kunin.[8] Two new exchange resins, one a carboxylic acid cation-exchanger and the second a strongly basic anion-exchanger have been introduced. The first absorbs basic amino-acids which are, however, more readily eluted than from the earlier more strongly acidic resins; the second can adsorb all except the most strongly basic amino-acids. A complete scheme of separation is outlined, using these in conjunction with a more weakly basic resin which absorbs only inorganic acids and dibasic amino-acids.

The principle of displacement development introduced by Tiselius has been adapted by Partridge and co-workers as a preparative method for the separation of amino-acids on ion-exchange columns. The aromatic acids are removed by adsorption on charcoal and the remainder of the amino-acids are adsorbed on a cation-exchange resin and successively displaced in groups by ammonia. The various groups are then refractionated.[8a, 8b, 8c]

It has been found, by H. Rinderknecht and C. Niemann,[9] that *N*-acetylamino-acids can be esterified without a catalyst, by heating with methanol under pressure to 180° C. The reactions of *N*-acylamino-acids, with particular reference to the formation of acid chlorides, have also been investigated by H. E. Carter and J. W. Hinman.[10] They found, in confirmation of previous work carried out in connexion with the synthesis of penicillin—and now published in the monograph[11]—that the reactions of *N*-alkoyl-amino-acids, on treatment with phosphorus halides, are best explained by the formation, not of an acid chloride, but of an oxazolone salt. Carbobenzoxy and toluenesulphonyl derivatives, on the other hand, gave acid chlorides and not oxazolones. These findings clear up previous anomalies found when using optically active

compounds, and are of importance in connexion with the synthesis of peptides.

Some attention has been paid to protective groups for use in the synthesis of peptides and phenylmercaptocarbonyl derivatives are suggested for this purpose by G. C. H. Ehrensvärd.[12] After condensation, the protective group is easily removed by treatment with lead salts. J. C. Sheehan and V. S. Frank[13] have used phthaloyl derivatives for this purpose, the phthaloyl group being removed at the end of the synthesis by treatment with hydrazine. Recent developments on the chemistry of phthalimides may be coupled with this method, to give a versatile and convenient method of peptide synthesis : these are the preparation of phthalyl derivatives of amino-acids reported previously[14]; and the observation made by H. J. Barber and W. R. Wragg[15] that the hydrazide method of decomposition leads directly to simple salts of the primary amines with phthalhydrazide.

The use of the *N*-carboxyanhydrides of amino-acids in peptide synthesis has been suggested by J. L. Bailey.[16]

R. L. M. Synge[17] has summarized the work on naturally occurring peptides, paying special attention to constitution where this is known, and to abnormal features of the molecule.

Sulphur-containing amino compounds: Methionine.—The now well-known method of synthesizing this amino-acid from the cyanohydrin of acrolein by addition of methyl mercaptan and hydrolysis has recently been made the subject of a patent[18], also a similar method from β-methylmercaptopropionaldehyde which is converted to the hydantoin by means of ammonium carbonate and sodium cyanide; the hydantoin is then hydrolysed to methionine.[19]

Cystine.—Two publications by M. W. Farlow[20] and H. Behrlinger[21] deal with the synthesis of cystine by the addition of thioacetic acid to α-acetamidoacrylic acid followed by hydrolysis of the diacetyl compound to cysteine.

Penicillamine.—Various methods of preparing this amino-acid, which is obtained by the hydrolysis of penicillin, are given in the monograph which has been published.[22] The original method of obtaining it by the addition of benzyl mercaptan to 4-*iso*propylidene-2-phenyloxazolone followed by hydrolysis and reductive removal of the benzyl group in liquid ammonia, was, in the course of the wartime work on penicillin, superseded by a better method in which *N*-chloroacetylvaline was converted by treatment with pyridine into 2-methyl-4-*iso*propylidene-oxazolone to which hydrogen sulphide was added in the presence of a catalyst, the free amino-acid then being prepared by acid hydrolysis.[23]

One of the methods mentioned in the monograph, using α-amino-β-β-dimethylacrylic acid, has led to an exhaustive research on the reactions of α-amino-acids and -nitriles with various sulphur compounds and has led to the discovery of new methods for the synthesis of many types of heterocyclic compounds. It was found that reaction between ethyl α-amino-β-β-dimethylacrylate and carbon disulphide gave 5 : 5-dimethyl-4-carbethoxythiothiazolid-2-one, which could be converted to penicillamine. Subsequently, in a widespread study of this reaction by Heilbron,

Cook and other collaborators, the reactions of amino-acids or nitriles with carbon disulphide, dithio-acids and *iso*thiocyanates led to new preparative methods for amino-acids, peptides, etc. This work has appeared in many papers in the *Journal of the Chemical Society* during the last three years, and has been summarized by Sir Ian Heilbron.[24] There he discusses the preparation of amino-acids from 2-mercapto-thiazolone which is itself obtainable in good yield from aminoacetonitrile and carbon disulphide. Since the date of that lecture, details of new methods mentioned in it for the synthesis of histidine from dithiohydantoin and 2-phenyl-4-ethoxymethyleneoxazol-5-one have been published by A. C. Davis and A. L. Levy.[25] An alternative method is also given in which 5-formyl-glyoxaline is condensed with 2-mercaptothiazol-5-one, and the condensation product converted to histidine in good yield by reduction and hydrolysis.

Threonine.—A paper has been published by K. Pfister, E. E. Howe, C. A. Robinson, A. C. Shabica, E. W. Pietrusza and M. Tishler[26] on modifications of an earlier synthesis of threonine from crotonic acid. It was found that *iso*crotonic acid gave better yields than crotonic acid in this method, and, also, that threonine was more readily accessible from amides of the higher melting modification of α-bromo-β-methoxybutyric acid, than from the free acid.

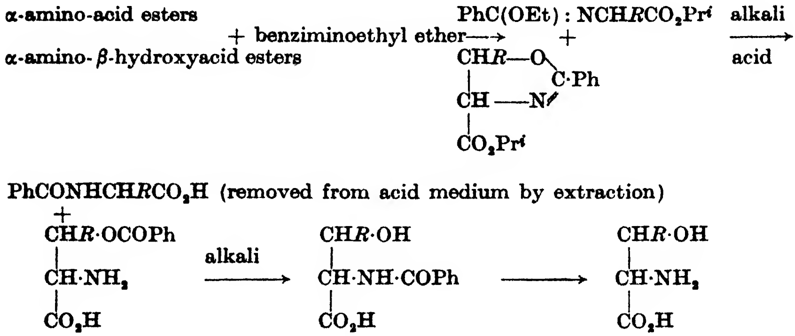
Further work on the formation of oxazolines from *N*-acylthreonines has been published by K. Pfister, C. A. Robinson, A. C. Shabica and M. Tishler,[27] and the method has been made the basis of a patent for the conversion of *allo*threonine to threonine *via* the oxazolines.[28]

D. F. Elliott[29] has now shown that *allo*threonine ethyl ester hydrochloride reacts with benziminoethyl ether under mild conditions to give *cis*-4-carbethoxy-2-phenyl-5-methyl-Δ^2-oxazoline, whereas the analogous threonine derivative gives the *trans*-oxazoline, both reactions having taken place without alteration of configuration. Both oxazoline carboxylic esters, however, on treatment with alkali, gave the same acid. This was converted by cold acid to *O*-benzoylthreonine, showing that the oxazoline carboxylic acid had the *trans* structure.

A simple separation of DL-threonine and DL-*allo*-threonine is described by Shabica *et al.* using sodium alkoxide.[29a]

These transformations have also been applied successfully by D. F. Elliott[30] to the very difficult problem of the isolation of threonine from proteins. After hydrolysis of the protein, glutamic acid, basic amino-acids and the less soluble neutral amino-acids were removed, as completely as possible, by the usual methods. The residual amino-acids were then converted to the *iso*propyl esters, these having previously been found to give higher yields of oxazolines than the ethyl esters on reaction with benziminoethyl ether, the next stage in the separation. This reaction gave oxazolines from serine and threonine and substituted imino-ethers from the remaining amino-acid esters. Subsequent alkaline hydrolysis converted the oxazoline esters to the carboxylic acids without ring-opening, and the imino-ethers derived from the other amino-acid esters to the *N*-benzoyl compounds. Acidification then opened the oxazolines to the *O*-benzoyl derivatives of serine and threonine, which are soluble in acid, and permitted removal of the benzoyl amino-acids by extraction.

The serine and threonine derivatives remaining in the aqueous acid were transformed into *N*-benzoyl derivatives by basification and removed from the re-acidified solution by extraction; acid hydrolysis to the parent amino-acids and chromatographic separation completed the process for the isolation of threonine and serine. It may be noted, in passing, that the serine obtained by this method is optically inactive. The method permits the isolation of 20% of the threonine originally present in the protein, and the reactions may be indicated thus :

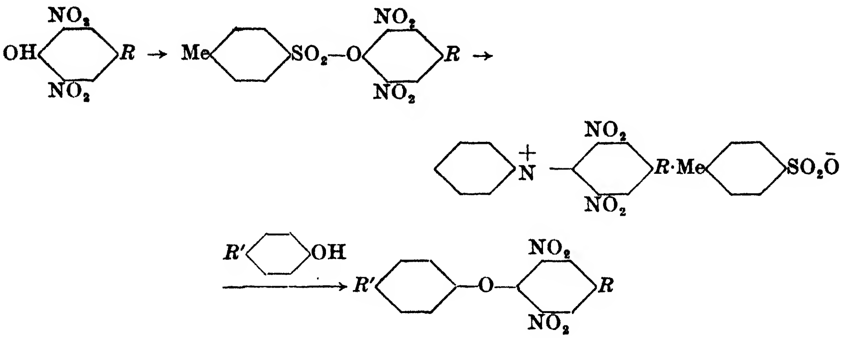


Tyrosine and thyroxine.—A series of papers has been published by B. A. Hems and colleagues[31] dealing with a new synthesis of thyroxine. Since, for many of the reactions contemplated, tyrosine was an important intermediate, methods for its preparation were first investigated, and a convenient modification of an older method is given. Several abortive attempts to prepare thyroxine by the iodination of thyronine are also mentioned, followed by an investigation of the possible use of dinitrodiphenyl ethers. 3 : 5-Dinitro-4-*p*-methoxyphenoxy-toluene and -benzoic acid methyl ester were used as models in these investigations, being prepared from the appropriate chlorodinitrobenzenes and quinol monomethyl ether in the usual way. The dinitrodiphenyl ethers were reduced to the diamino compounds, and it was found that these could be converted to the corresponding di-iododiphenyl ethers by tetrazotization in anhydrous acid solutions, followed by decomposition with aqueous solutions of iodides.

The synthesis of thyroxine was then completed from 3 : 5-di-iodo-4-*p*-methoxyphenoxybenzoic acid methyl ester through the aldehyde and condensation of this with hippuric acid.

In the second paper, methods of preparing diphenyl ethers from dinitrophenols were exhaustively examined. The dinitrophenols were first converted into the chloro-compounds and then the dinitrodiphenyl ethers. An alternative method which gave better yields was later found. In this the quaternary salts obtained by the treatment of the tosyl esters of dinitrophenols with tertiary bases, of which pyridine was found to be the most convenient, were found to give dinitrodiphenyl ethers on treatment with phenols. In this way 3 : 5-dinitro-4-*p*-methoxytoluene and similar compounds were directly obtained from dinitrocresol, etc. without isolation of the toluenesulphonyl ester or of the quaternary salt. A

number of examples were given and the general reaction is as shown below:



In the third paper a route was selected, using 5-*p*-hydroxybenzyl-hydantoin. This was nitrated and the dinitro compound converted to 5-(3′ : 5′-dinitro-4′-*p*-methoxyphenoxybenzyl)-hydantoin by the above method. Catalytic reduction, conversion of the diamino- to the di-iodo compound by tetrazotization in an anhydrous solution, and treatment with iodide gave 5-(3′ : 5′-di-iodo-4′-*p*-methoxyphenoxybenzyl)-hydantoin. This was hydrolysed in two stages to di-iodothyronine and the synthesis of thyroxine completed by iodination. By these reactiins thyroxine was obtained in 14% over-all yield from *p*-hydroxybenzaldehyde.

The fourth paper deals with analytical methods in this field, with particular reference to the differential analysis of thyroxine and di-iodotyrosine by polarographic methods. In a later paper[32] the same group of workers examined the possibility of using the above methods on L-tyrosine and found that, when 3 : 5-dinitro-*N*-acetyl-L-tyrosine ethyl ester was used as an intermediate, it was possible to complete the synthesis to give optically active L-thyroxine directly in 25% over-all yield.

p-Aminosalicylic acid (P.A.S.)

The Medical Research Council has recently reported[33] on the value of P.A.S. in association with streptomycin for the treatment of acute progressive pulmonary tuberculosis. Trials proved unequivocally that the combination of P.A.S. with streptomycin reduced considerably the risk of development of streptomycin-resistant strains of tubercle bacilli.

Since the dosage is 20 g. per day for each patient, there is considerable interest both in the economic manufacture of P.A.S. itself and in the search for more effective related substances. There is little doubt that the carboxylation of *m*-aminophenol by means of alkali carbonates and carbon dioxide under pressure is the method of choice and this is being reported in chemical literature[34,35,36] and claimed in patents.[37,38] The most interesting feature is the Italian statement that high yields can be obtained at atmospheric pressure.[39] This paper also describes the method

from 4-nitro-2-aminobenzoic acid *via* the diazonium salt to 4-nitro-salicylic[40] which is reduced to P.A.S. and the route from 2 : 4-dinitrophenylacetic acid *via* 5-nitrobenzisoxazole-2-carboxylic ester.[41] The latter is the subject of a patent application from the Swedish Ferrosan Akt.[42] though its main interest lies in the fact that isomeric products are precluded. Ferrosan also claim a method of preparing the pure sodium salt in alcoholic suspension.[43]

The Swiss workers H. Erlenmeyer *et al.* also tested against tuberculosis several other 2 : 4-disubstituted benzoic acids, including 2 : 4-diaminobenzoic acid and also 2-amino-4-hydroxybenzonitrile. None of the compounds was as active as P.A.S. Some derivatives and analogues of P.A.S. were examined by D. J. Drain, C. L. Goodacre and D. E. Seymour[44] for *in vitro* activity against the tuberculosis organism. Esters were highly active, amides and ethers much less so. The only substituted P.A.S. tested was 3 : 5-di-iodo-4-amino-2-hydroxybenzoic acid, which was found to be highly active. It is of interest to note, in view of other work, that 4-aminosalicylaldehyde thiosemicarbazone was also highly active.

A Scandinavian group, Jensen *et al.*,[45] have also examined a number of esters and amides of P.A.S., obtained by catalytic reduction of the corresponding nitro compounds,[46] and find them to have activity comparable with P.A.S. The direct esterification of P.A.S. using BF_3 as catalyst has recently been described.[47]

There is also a long paper by R. Hirt and H. Hurni[48] in which a large number of compounds related to P.A.S. were tested. These were mostly either position isomers, all of which were much less active, or derivatives of P.A.S. in which the amino group was substituted by an acyl, carbalkoxy or arylsulphonyl group. Several of the *N*-acyl derivatives were highly active *in vitro*, and it was pointed out that they might be worthy of further examination, since they might not be excreted as rapidly as P.A.S. itself.

In two papers H. Erlenmeyer *et al.*[49] examined various types of amines which have been shown to have antitubercular activity, with a view to suggesting constitutional influences, such as mesomerism, which might have a bearing on their activity.

References

[1] *Helv. chim. Acta*, 1948, **31**, 1617
[2] Ibid., 2088
[3] *Helv. chim. Acta*, 1949, **32**, 1034
[4] Ibid., 1156
[5] Ibid., 1936
[6] Ibid., 333; *Helv. chim. Acta*, 1948, **31**, 1908
[7] *J. biol. Chem.*, 1949, **179**, 1169; ibid., 180, 473
[8] *Ind. Eng. Chem.*, 1949, **41**, 460
[8a] Partridge, S. M. and Westall, R. G., *Biochem. J.*, 1949, **44**, 418
[8b] Partridge, S. M. and Brimley, R. C., ibid., 513
[8c] Partridge, S. M., ibid., 521
[9] *J. Amer. chem. Soc.*, 1948, **70**, 2605
[10] *J. biol. Chem.*, 1949, **178**, 403
[11] 'Chemistry of Penicillin,' chap. 21
[12] *Nature*, 1947, **159**, 500
[13] *J. Amer. Chem. Soc.*, 1949, **71**, 1856
[14] Annual Reports, 1948, **33**, 587

[15] *J. chem. Soc.*, **1947**, 1331
[16] First International Congress of Biochemistry, Abstracts of Communications, 225 *Nature*, 1949, **164**, 889
[17] *Quart. Rev. chem. Soc.*, 1949, **3**, No. 3, 245
[18] B.P. 605,311
[19] B.P. 630,139
[20] *J. biol. Chem.*, 1948, **176**, 71
[21] *Chem. Ber.*, 1948, **81**, 326
[22] 'Chemistry of Penicillin,' chap. 16
[23] *See also* B.P. 627,768
[24] *J chem. Soc.*, **1949**, 2099
[25] Ibid., 2179
[26] *J. Amer. chem. Soc.*, 1949, **71**, 1096
[27] Ibid., 1101
[28] B.P. 626,359
[29] *J. chem. Soc.*, **1949**, 589
[29a] U.S.P. 2,461,847
[30] *Biochem. J.*, 1949, **45**, 429
[31] *J. chem. Soc.*, **1949**, S185, S190, S199, S204
[32] Ibid., 3424
[33] *Brit. med. J.*, 1949, ii, 1521
[34] *J. chem. Soc.*, **1949**, 1498
[35] *Helv. chim. Acta*, 1948, **31**, 988
[36] *Monatsh.*, 1949, **80**, 197
[37] Labo. Franç de Chimiotherapie, B.P. Appl. No. 15,992/48
[38] A. Wander, A.G., B.P. Appl. Nos. 20,373/48, 13,873/49
[39] *Justoni, Terrizi e Pirola, Farm. Sci.e.tech.* (*Pavia*), 1948, **3**, 509 (through *Chem. Abs.*, **42**, 7273e)
[40] U.S.P. 2,445,242 ; B.P. 623,114
[41] McGhie, J. F., Morton, C., Reynolds, B. L. and Spence, J. W., *J. Soc. chem. Ind.*, 1949, **68**, 328
[42] B.P. Appl. No. 4,597/47
[43] B.P. Appl. No. 6,011/49
[44] *J. Pharm. Pharmacol.*, 1949, **1**, 784
[45] *Acta. chem. scand.*, 1948, **2**, 228
[46] B.P. Appl. No. 2,183/49
[47] *J. Amer. chem. Soc.*, 1949, **71**, 3564
[48] *Helv. chim. Acta*, 1949, **32**, 378
[49] Ibid., 605, 1275

TROPICAL MEDICINE (L. P. Walls, M.A., Ph.D.)

The Wellcome Research Laboratories, Chemical Division.

In this field much of the promise of earlier years was confirmed in 1949. The most notable discovery reported during the year was that of 'Antrycide', to which brief reference was made in last year's Report. The hope was expressed that this drug would solve the chief economic problem of tropical Africa—bovine trypanosomiasis. H. E. Hornby[1] has published an interesting review of our present knowledge of the animal trypanosomiases. The importance of the new antibiotic, chloramphenicol ('Chloromycetin'), now available by a synthetic process, for the treatment of scrub typhus has been established ; it is also highly effective in typhoid fever. Extended trials have confirmed the value of miracil ('Nilodin') in the treatment of schistosomiasis, and of hetrazan ('Banocide') for filarial infections. No outstanding new antimalarial was announced in

1949, but a biological discovery of first-class importance, namely the actual demonstration of the long-postulated pre-erythrocytic forms of the human parasites, *Plasmodium vivax* and *P. falciparum*, in the liver by H. E. Shortt and his collaborators, has led to a better understanding of the rationale of the chemotherapy of this complex disease. This aspect of the discovery has been ably elucidated by N. H. Fairley[2] in his authoritative Croonian lectures. In 1949 as in previous years the number of papers published on different aspects of the malaria problem greatly exceeded that on any other tropical disease. Although with the end of the war the extreme urgency diminished, it remains probably the world's chief medical problem. The notable success achieved by the three modes of attack—prevention by sanitation methods, prophylaxis by suppressants, and clinical treatment by drugs—is evidenced in these publications.

Organic antimony compounds continue to be used in many tropical diseases, for example, schistosomiasis, kala-azar, filariasis, and a welcome account of their development has been given by H. Schmidt,[3] the leading worker in this field.

Malaria.—Owing to the brilliant work of H. E. Shortt and his colleagues knowledge of the life-cycle of the malaria parasites is now almost complete, and a proper understanding of antimalarial drugs is dependent on this knowledge. N. H. Fairley[2] depicts the development of *Plasmodium vivax*, the parasite of benign tertian malaria, after infection by mosquito bite, as follows:

$$\begin{tikzcd}
 & \begin{array}{c}\text{(Primary malaria)}\\ \text{Erythrocytic schizogony } (\rightarrow \text{schizonts}) \\ \text{(C)}\end{array} & \begin{array}{c}\text{(Relapse)}\\ \text{Erythrocytic schizogony (E)}\end{array} \\
\begin{array}{c}\text{Sporozoite}\\ \text{(A)}\end{array} \arrow[r] & \begin{array}{c}\text{Pre-erythrocytic}\\ \text{schizogony}\\ \text{(B)}\end{array} \arrow[u] \arrow[r] & \begin{array}{c}\text{Exo-erythrocytic}\\ \text{schizogony}\\ \text{(D)}\end{array} \arrow[u]
\end{tikzcd}$$

and of *P. falciparum* (malignant tertian) as follows:

$$\begin{tikzcd}
 & \begin{array}{c}\text{(Primary malaria and recrudescences)}\\ \text{Erythrocytic schizogony (C)}\end{array} \\
\begin{array}{c}\text{Sporozoite}\\ \text{(A)}\end{array} \arrow[r] & \begin{array}{c}\text{Pre-erythrocytic schizogony}\\ \text{(B)}\end{array} \arrow[u]
\end{tikzcd}$$

Different drugs may attack the parasite at different stages of development, and their usefulness in prevention and treament is thus determined. Quinine, mepacrine, sontochin (I), chloroquine (II), proguanil (paludrine) (VI), and certain sulphonamides are schizonticidal-suppressants, because they prevent overt attacks of malaria by killing the schizonts (C) as they appear in the blood. Proguanil also acts as a causal prophylactic for *P. falciparum* and a partial causal prophylactic for *P. vivax* malaria by attacking the pre-erythrocytic forms (B). As schizonticides these drugs can effect radical cure of clinical *P. falciparum* malaria, but with *P. vivax* malaria they cannot prevent relapses, which are a consequence of the by-pass [(B) → (D) → (E)]. For this purpose pamaquin or the related less-toxic pentaquine (VII), which acts on the exo-erythrocytic form (D), must be used. In addition, pamaquin and proguanil have a gametocidal

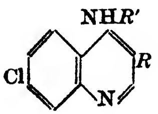
action against all three human parasites, and thus prevent infection of mosquitoes. Chloroquine is the most powerful schizonticide, and has the further advantage over mepacrine of not staining the skin. Proguanil is less rapid in action but has very low toxicity. Proguanil-resistance can be induced in the laboratory and may be encountered in practice ; but 2000-fold resistant strains are still susceptible to chloroquine and pentaquine.[4] The oustanding problem in the chemotherapy of malaria is to replace the dangerously toxic pamaquin group by a safe drug active against the exo-erythrocytic forms of *P. vivax*.

Much of the American antimalarial effort was a development of the pre-war German work on acridines and quinolines carrying a basic side-chain, which had produced pamaquin, mepacrine, chloroquine ('resochin'),[5] endochin,[6] which is said to be highly active against exo-erythrocytic forms of bird malaria, and on various sulphonamides.[7] In addition to drugs already mentioned the American work has produced 'Camoquine' (III), oxychloroquine (IV), *iso*pentaquine (VIII), and metachloridine (IX), which have received extended trials, as also have the nivaquines (V). 'Camoquine' shows considerable promise as a schizonticide. This work forms the subject of numerous papers and patents and is collected together in 'The Survey of Antimalarial Drugs' (Wiselogle, 1946). W. C. Cooper[7a] summarizes current American assessments on the more established drugs and notes that oxychloroquine, 'Camoquine' and *iso*pentaquine are not commercially available. In the patent literature are descriptions of quinolines analogous to 'Camoquine'[8] and to pamaquin,[9] of acridines analogous to 'Camoquine'[10] and mepacrine,[11] and of various sulphonamides claimed as antimalarials.[12]

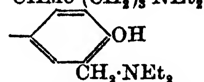
The original manufacturing process for chloroquine is described in detail by R. L. Kenyon, J. A. Wiesner and C. E. Kwartler,[13] but this was made obsolete by the later American work already published but now issuing in patents. The essential feature is the replacement of oxalo-acetic ester by ethoxymethylenemalonic ester or its equivalent in building the intermediate, 7-chloro-4-quinolone. This process has the all-important technical advantage of not producing significant quantities of the unwanted isomer, 5-chloro-4-quinolone, as a by-product.[13a] Later developments by H. R. Snyder and R. E. Jones avoid isolation of ethoxymethylene-malonic (or cyanacetic) ester by heating all three reagents—orthoformic ester, malonic ester and amine—together.[13b] A simplified process for mepacrine is claimed by G. L. Shaw and R. G. Jones[14] and a single-stage synthesis of pamaquin from the quinoline moiety and 1-diethylamino-4-pentanone by Japanese workers.[14a] The work of the I.C.I. team was first on basically substituted pyrimidines among which many active anti-malarials were found[15] ; this work culminated in the discovery of proguanil of which several manufacturing processes are described by F. H. S. Curd, F. L. Rose and their co-workers.[16] A new approach was also made by L. F. Fieser and his collaborators,[17] who found considerable activity including an effect on exo-erythrocytic forms of the parasite in certain naphthoquinones, of which (X) is the most promising. Many aspects of this antimalarial activity have been investigated : correlation of structure and activity, physical properties of the drugs, metabolism, and enzyme action. In contrast to their effect in the acridine and quinoline series,

introduction of methoxyl or halogen into the 6-position of 2-hydroxy-3-alkyl-1 : 4-naphthoquinones destroys the activity.[18]

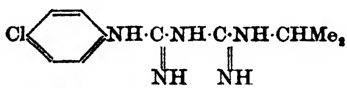
In 1949 the preparation of further analogues of pamaquin has been described without uncovering a superior drug.[19] An analogue of chloroquine, 7-chloro-4-(1-methyl-4 : 1′-pyrrolidylbutylamino)-quinoline, has similar activity.[20] Further papers on the synthesis of diguanides have been published by F. H. S. Curd, F. L. Rose and their collaborators.[21] Considerable activity has also been found in 2- and 2 : 6-dichloro-3-dialkylaminoalkylaminoquinoxalines,[22] and in carbinolamines derived from 6 : 7-dimethylquinoline.[23] E. A. Falco, G. H. Hitchings, P. B. Russell, and H. Vander Werff[24] attempt to correlate antimalarial activity and inhibition of growth of *Lactobacillus casei* (pteroylglutamic acid antagonism); in fact, proguanil is an inhibitor of *L. casei*, whereas the much more powerful inhibitor, 2 : 4-diamino-5-*p*-chlorophenoxypyrimidine, which has a certain structural analogy to proguanil, is about equal to quinine against *P. gallinaceum* infections in chicks.



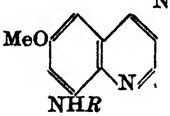
(I) R = Me; R' = $CHMe{\cdot}(CH_2)_3{\cdot}NEt_2$
(II) R = H; R' = $CHMe{\cdot}(CH_2)_3{\cdot}NEt_2$
(III) R = H; R' =



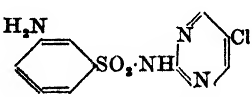
(IV) R = H; R' = $CH_2{\cdot}CHOH{\cdot}CH_2{\cdot}NEt_2$
(V) R = H or Me; R' = $(CH_2)_2{\cdot}NEt_2$



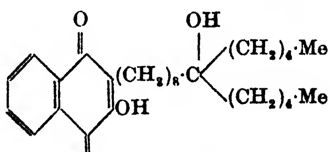
(VI)



(VII) R = $(CH_2)_6{\cdot}NHCHMe_2$
(VIII) R = $CHMe{\cdot}(CH_2)_3{\cdot}NHCHMe_2$



(IX)



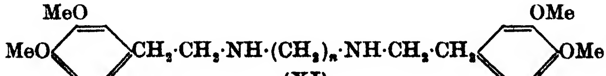
(X)

Amoebiasis.—Intestinal infections due to *Entamoeba histolytica* have long been treated with the ipecacuanha alkaloid, emetine (or its sparingly soluble bismuthiodide : EBI), which is a highly effective drug, but suffers from the disadvantage of causing unpleasant side-reactions often in therapeutic doses. Recently another alkaloid, conessine, has been used, both in intestinal amoebiasis, and also in the usually intractable hepatic abscess with considerable success, even in emetine-resistant cases. An account has been published[25] of preliminary work on the chemistry of this alkaloid, which is a steroid with one ethylenic linkage, a dimethylamino group, a cyclic methylimino group, and probably a 5-*allo*pregnane structure. The structure of emetine has received renewed attention, particularly from H. T. Openshaw and his collaborators.[26] The literature on this subject has been reviewed by M. M. Janot.[27] Particularly for

chronic cases halogenated quinolines, such as 7-iodo-8-hydroxyquinoline-5-sulphonic acid (chiniofon, yatren, quinoxyl), and 5 : 7-diiodoquinoline (diodoquin), have proved of value. A beneficial effect on the course of the disease is also exerted by certain organic arsenicals, notably *p*-ureidophenylarsonic acid (carbarsone) and 3-acetamido-4-hydroxyphenylarsonic acid (acetarsone).

In a preface to an extended research for new amoebicides, L. G. Goodwin, C. A. Hoare and T. M. Sharp[28] discuss the status of these drugs, and conclude that improved drugs are required. The next paper describes the synthesis and testing of a large number of amines formally related to emetine, of which the best [(XI) ; $n = 6$–10] are much less active than emetine; although less toxic they were too irritant for clinical trial. Further synthetic work was based on Pyman's compound (XII),[29] which is formally analogous to the trypanocide, 1 : 11-diamidinoundecane; consequently analogues related to (XII) in the same sense as stilbamidine, propamidine, and pentamidine are to the latter, were prepared.

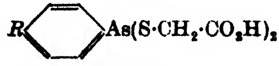
The difficulty of experimental evaluation of potential amoebicides is stressed by other authors.[30] Activity *in vitro* was found in a wide range of substances, particularly arsenicals, but only a few showed promise *in vivo*, namely in man carbarsone oxide (*p*-ureidophenylarsenoxide), and in monkeys its thio-derivates bis(carbethoxymethylmercapto)arsino-*p*-phenylurea [(XIII) ; $R = NH{\cdot}CO{\cdot}NH_2$] and bis(*o*-carboxyphenylmercapto)arsino-*p*-phenylurea, the last-named being the least toxic. Favourable clinical results have recently been described[30a] but doubts have been expressed[30b] on the advantages of these thioarsenites over the parent arsenical carbarsone, which is itself not entirely satisfactory. Bismuth glycolyl arsanilate, originally prepared by Hermann at Höchst during the war,[30c] has also been the subject of successful clinical trials in the U.S. under the name 'Milibis' (Win 1011) according to a preliminary report.[30d] A test method using dogs has been recently described[31]; cures were obtained with the recognized amoebicides, except emetine, and chloroquine, penicillin, streptomycin, and sulpha drugs were also ineffective. Bacterial infection often aggravates amoebic dysentery and hence associated treatment with penicillin or sulphaguanidine is advantageous. Recently an acute chance observation by L. V. McVay, R. L. Laird and D. H. Sprunt[32] led to the discovery of the potential value of the new antibiotic, aureomycin, in the treatment of amoebic dysentery, and further information will be awaited with interest.



(XI)

$(C_5H_{11})_2N{\cdot}(CH_2)_{10}{\cdot}N(C_5H_{11})_2$

(XII)



(XIII)

Filariasis.—Interest in this mosquito-borne helminth infection, which is endemic in the Pacific Islands, was aroused during the war, and the consequent research was rewarded by the discovery of 'Hetrazan' (1-diethylcarbamyl-4-methylpiperazine).[33] This drug, which is administered

orally, effects radical cure of the disease, causing rapid disappearance of microfilariae from the blood and sterilization or death of the adult worms. It has been marketed as the citrate under the name 'Banocide.' R. I. Hewitt[34] has described the mass treatment of the inhabitants of St. Croix (American Virgin Islands) with 'Hetrazan' as a control measure for Bancroftian filariasis. In all cases examined, parasitaemia was reduced to values no longer infective for mosquitoes, and this process appears to hold high promise for isolated communities. The course of onchocerciasis,[35] a frequent cause of blindness in Africa, and of loasis[36] are also favourably influenced by hetrazan but less dramatically and with allergic reactions. A method of estimation of hetrazan in body fluids has been described.[37] Patents for the manufacture are beginning to appear in the name of American Cyanamid Co.[37a]

A full and authoritative account of the chemotherapy of filariasis has been published by American workers.[38] The use of the cotton-rat and dog as experimental animals is described, and drugs are discussed under four groups: arsenicals, antimonials, cyanines, and piperazines. The best arsenical is bis(carboxymethylmercapto)arsino-*p*-benzamide [(XIII); $R = CO{\cdot}NH_2$], but requires intravenous injection, is less effective than hetrazan, and may cause toxic symptoms. Anthiomaline, the lithium antimony salt of thiomalic acid, also reduces the microfilariae, but fails to effect radical cure. A most interesting discovery was that of the activity of cyanines and related compounds. The greatest activity was found in 1:1′-bis-β-ethoxyethyl-2:2′-carbocyanine chloride or *p*-toluene-sulphonate, but radical cure was not effected in a human case, and toxic symptoms intervened. More recent work by L. Peters and his colleagues[39] suggests that (1-amyl-2:5-dimethyl-3-pyrrole) (1:6-dimethyl-2-quinoline)-dimethincyanine chloride is a superior drug. A new advance in the chemotherapy of filariasis may result from the work of W. E. Kershaw, J. Williamson and D. S. Bertram,[40] who examined the prophylactic action of drugs already known to protect against trypanosomes. Antrypol and stilbamidine were useless, but *p*-melaminylphenylstibonate afforded protection for at least three weeks.

Leprosy.—The acceptance of Hansen's acid-fast bacillus as the causative parasite suggested, in the absence of a direct experimental method of assessment, that drugs of promise in the treatment of tuberculosis might have a place in leprosy therapy. The sulphones have shown great promise, and according to E. A. Sharp and E. H. Payne,[41] whereas promin is too toxic and promizole useful but too toxic, diasone and sulphetrone(XIV)[42] are satisfactory with the latter the drug of choice. Treatment involves prolonged administration of considerable quantities of drug under close supervision, but provided the problem of expense can be overcome new hope has arisen for the multitude of sufferers from this dread disease. Rather unexpectedly streptomycin, much the more efficient drug in tuberculosis, is of little value in leprosy.[43] The older rather unpleasant remedy—heavy dosage with esters of hydnocarpus and chaulmoogric acids—still has advocates particularly for certain manifestations of the disease. Chemical interest has been aroused by a new naturally occurring remedy, asiaticoside, which on hydrolysis furnishes D-glucose, L-rhamnose, and a triterpene pentacyclic asiatic acid.[44]

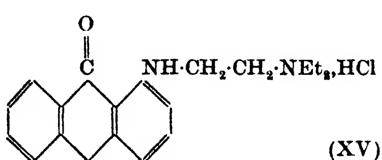
$$[C_6H_5\cdot \underset{\displaystyle SO_3Na}{\underset{|}{CH}}\cdot CH_2\cdot \underset{\displaystyle SO_3Na}{\underset{|}{CH}}\cdot NH\cdot C_6H_4]_2SO_2 \quad p$$

(XIV)

Schistosomiasis disputes with malaria the reputation of being the most prevalent human disease, and is responsible for an enormous amount of ill-health in many parts of the world. Until recently the only remedies were antimonials, which entailed intravenous injection, not suited to mass treatment in the tropics, and the risk of serious toxic symptoms. The discovery of the miracils by German workers[45] has made possible effective oral treatment in Egypt and S. Rhodesia. The miracils A, B, C, and D are xanthone and thioxanthone derivatives of which the order of activity is markedly different in infected mice and monkeys. For human disease miracil D ('Nilodin') (XV) has been successfully used in *Schistosoma haematobium* infections, but with frequent failures with *S. mansoni*. The miracils are also inactive in experimental *S. japonicum* infections.

Valuable information on the method of testing drugs for schistosomicidal activity has been given by M. Schubert, who applied his method to over 400 compounds of which the most promising were certain oil-soluble thioantimonials of the general formula $(RS)_3Sb$.[47] As a contribution to testing method, O. D. Standen[48] has examined the desiderata for successful establishment of colonies of the snail vector. Several claims of schistosomicidal activity await confirmation. The amino-group of certain sulpha-drugs has been replaced by a stibonic acid residue, and it is claimed[49] that *p*-sulphonamidobenzenestibonic acid has some activity in *S. mansoni* infection in mice. Two compounds related to pamaquin, namely 8-di*iso*butylaminoethylamino- and 6-methoxy-8-di*iso*butylamino-*iso*propylamino-quinoline, are also said to be active in this infection.[50]

With a view to preventive measures, F. J. Schreiber and M. Schubert[51] have examined the effect of numerous substances on the cercariae of *S. mansoni*, which are released into water by infected snails and thence enter the human host; aromatic quinones, which are known enzyme inhibitors and certain tertiary amines, such as methyldi-γ-phenoxypropylamine, kill cercariae extremely rapidly even at a concentration as low as 0 01%.



(XV)

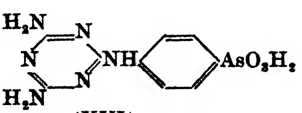
Trypanosomiasis.—Many aspects of the trypanosomiasis problem in Africa have been dealt with in recent publications of H.M. Stationery Office.[52] Little information is yet available on 'Antrycide,'[53] but it is clear that the drug is notable for its activity against a wide range of species, and for its prophylactic properties. Unfortunately there is evidence[54] that trypanosomes rapidly acquire resistance to 'Antrycide,' and the resistant strains are also resistant to dimidium bromide, the phenanthridinium drug that has been used for the treatment of the bovine

disease for some years. The usefulness of 'Antrycide' as a prophylactic is thus rendered doubtful. A new method of synthesis of phenanthridine compounds has been described by J. Cymerman and W. F. Short,[55] and notable improvements in the manufacture of dimidium bromide by H. J. Barber.[56] 1-Phenyl*iso*quinolinium salts, closely analogous to the active phenanthridines, were only slightly active.[57]

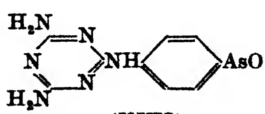
In human trypanosomiasis in Africa the most notable recent work has been in mass prophylaxis, sometimes by Bayer 205 (suramin), but more usually by propamidine or pentamidine. The possibility of oral prophylaxis has been indicated by L. Launoy,[58] who has demonstrated a protective effect in experimental animals of the insoluble methylenebishydroxynaphthoate of pentamidine. Synthetic work in the diamidine field continues. Introduction of substituents in the *ortho*-position to the ether linkage of 4 : 4′-diamidino-$\alpha:\omega$-diphenoxyalkanes did not increase the trypanocidal activity, although halogen caused a pronounced increase in antibacterial activity.[59] *p*-Phenylenediguanide also has trypanocidal activity, but to a much less degree than stilbamidine.[60] The increased toxicity and reduced effectiveness of stilbamidine after storage of the solution have been the subject of much study; J. D. Fulton and T. W. Goodwin[61] conclude that partial hydrolysis to 4-carbamyl-4′-amidino- and 4 : 4′-dicarbamylstilbene occurs, both of these artefacts being inactive against *Trypanosoma congolense* and *T. rhodesiense*.

The work of E. A. Friedheim on the synthesis of melaminyl derivatives of phenylarsonic acid[62] has culminated in clinical trials in Africa; both melarsen (XVI) and melarsen oxide (XVII), which are effective orally, are as active against tryparsamide-resistant strains of *T. rhodesiense* as against the parent strain.[63] It is suggested that, although (XVII) has the same lethal action on trypanosomes as other arsenoxides, its means of fixation or of entry into the trypanosome cell is different, and that these factors are concerned in drug-resistance. An alkylmercapto-derivative of (XVII), 'Mel B' [cf. (XIII)], has been successfully used in secondary trypanosomiasis, which involves the central nervous system.[64]

Attempts to synthesize new trypanocides continue. Ciba, Ltd.[65] claim that 2:2′-(4:4′-diphenylene)-diminazolines are trypanocidal parentally or orally, and are of low toxicity. *p*-Arsonosobenzoyl derivatives of 2-aminothiazoles, 2-aminopyridine, and other heterocyclic amines have been prepared, but are of low activity.[66] Other work on organic arsenicals has also not led to notable success.[67] F. C. Goble has examined analogues of Bayer 7602 and of pamaquin in *T. cruzi* infections of mice and dogs; pentaquine was found to be markedly active.[68]



(XVI)



(XVII)

References

[1] *Vet. Rec.*, 1949, **61**, 375
[2] *Brit. med. J.*, 1949, ii, 825, 891
[3] *Angew. Chem.*, 1948, **60**, 261

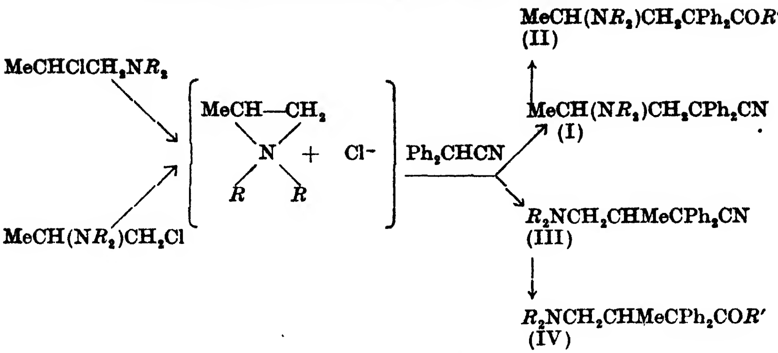
[4] Schmidt, L. H., Genther, C. S., Fradkin, R., and Squires, W., *J. Pharmacol.*, 1949, **95**, 382
[5] Andersag, H., *Chem. Ber.*, 1948, **81**, 499; D.R.P. 683,692
[6] Salzer, W., Timmler, H., Andersag, H., *Chem. Ber.*, 1948, **81**, 12
[7] Behnisch, R., ibid., 297
[7a] *U.S. Public Health Reports*, 1949, **64**, 717
[8] Parke Davis & Co., U.S.P. 2,474,818, 2,474,820–3
[9] Eli Lilly & Co., B.P. 597,816, 597,820, 600,827, 602,332
[10] Parke Davis & Co., U.S.P. 2,474,819, 2,474,824, B.P. 603,533
[11] Eli Lilly & Co., B.P. 602,351, 604,375, 605,393, 614,164
[12] American Cyanamid Co., B.P. 615,328; F. J. Wolf and Merck & Co., U.S.P. 2,473,931
[13] *Ind. Eng. Chem.*, 1949, **41**, 654
[13a] Price, C. C., Roberts, R. M., and Herbrandson, H. F., B.P. 627,297
[13b] B.P. 630,860; 631,110
[14] U.S.P. 2,459,777
[14a] Jap. Pat. 174,952
[15] B.P. 587,550, 590,706, also Parke Davis & Co., U.S.P. 2,455,396
[16] B.P. 599,714, 603,070, 607,720, 618,613, 619,497–8
[17] *J. Amer. chem. Soc.*, 1948, **70**, 3151 and following papers
[18] Fieser, L. F. and Brown, R. H., ibid., 1949, **71**, 3615
[19] Ibid., 455, 554, 2041, 2425
[20] Reitsema, R. H. and Hunter, J. H., ibid., 750
[21] *J. chem. Soc.*, **1949**, 98, 475, 1732, 1739, 2556, 2561
[22] Crowther, A. F., Curd, F. H. S., Davey, D. G. and Stacey, G. J., ibid., 1260
[23] Curd, F. H. S., Davey, D. G. and Stacey, G. J., ibid., 1271; King, H. and Wright, J., *Proc. roy. Soc.*, 1948 [B], **135**, 271
[24] *Nature*, 1949, **164**, 107
[25] Haworth, R. D., McKenna, J. and Nazar Singh, *J. chem. Soc.*, **1949**, 831
[26] Battersby, A. R. and Openshaw, H. T., ibid., S59, S67
[27] *Bull. Soc. chim. Fr.*, 1949, **16** (V), 185
[28] *Brit. J. Pharmacol.*, 1948, **3**, 44 and following papers
[29] *Chem. & Ind.*, **1937**, 789
[30] Anderson, H. H., Johnstone, H. J. and Hansen, E. L., *Amer. J. trop. Med.*, 1947, **27**, 153
[30a] Anderson *et al.*, *J. Amer. med. Ass.*, 1949, **140**, 1251;
[30b] *Lancet* (Annotation), 1949, ii, 803
[30c] BIOS Final Report No. 116, p. 54
[30d] *Chem. Engng. News*, 1949, **27**, 2863
[31] Thompson, P. E. and Lilligren, B. L., *Amer. J. trop. Med.*, 1949, **29**, 323
[32] *Science*, 1949, **109**, 590; *J. Amer. med. Ass.*, 1949, **140**, 1344
[33] Stewart, H. W., Turner, R. I., Denton, J. J., Kushner, S., Brancone, L. M., McEwen, W. L., Hewitt, R. I. and Subbarow, Y., *J. org. Chem.*, 1948, **13**, 134, 144
[34] *Nature*, 1949, **164**, 1135
[35] Hawkings, F. and Laurie, W., *Lancet*, 1949, **257**, 146; *The Times*, 1950, Jan. 5th, p. 5
[36] Murgatroyd, F. and Woodruff, A. W., *Lancet*, 1949, **257**, 147
[37] Lubran, M., *Nature*, 1949, **164**, 1135
[37a] B.P. 631,685, B.P. Appl. Nos. 736/49, 6711/49
[38] *Ann. N.Y. Acad. Sci.*, 1948, **50**, 19
[39] Peters, L., Bueding, E., Valk, A. D., Higashi, A., and Welch, A. D., *J. Pharmacol.*, 1949, **95**, 212
[40] *Brit. med. J.*, 1949, i, 130
[41] *Internat. J. Leprosy*, 1948, **16**, 157
[42] Gray, W. H. and Henry, T. A., B.P. 491,265
[43] Chaussinaud, R., Paris, C. and Crougue, O., *Bull. Soc. Path. exot.*, 1948, **41**, 573
[44] Boiteau, R., Buzas, A., Lederer, E. and Polonsky, J., *Bull. Soc. Chim. Biol.*, **1949**, **31**, 46; *Nature*, 1949, **163**, 258
Bhattacharyya, S. C., Lythgoe, B. and Trippett, S., ibid., 259
[45] Mauss, H., *Chem. Ber.*, 1948, **81**, 19; Kikuth, W., Gönnert, R. and Mauss, H., *Naturwissenschaften*, 1946, **33**, 253

[46] *Amer. J. trop. Med.*, 1948, **28**, 137; 1949, **29**, 115
[47] Clemence, L. W. and Leffler, M. T., *J. Amer. chem. Soc.*, 1948, **70**, 2439
[48] *Ann. trop. Med. Parasit.*, 1949, **43**, 13
[49] Englert, R. D. and Sweeting, O. J., *J. Amer. chem. Soc.*, 1948, **70**, 2977
[50] *Fed. Proc.*, 1949, **8**, 275
[51] *J. Parasitol.*, 1949, **35**, 364
[52] Buxton, P. A., 'Trypanosomiasis in Eastern Africa'; Davey, T. H., 'Trypanosomiasis in British West Africa'; Nash, T. A. M., 'Tsetse Flies in British West Africa'
[53] Curd, F. H. S. and Davey, D. G., *Nature*, 1949, **163**, 89
[54] Wilson, S. G., ibid., 873; *Vet. Rec.*, 1949, **61**, 395
[55] *J. chem. Soc.*, **1949**, 703; B.P. 614, 072
[56] B.P. 611,745, 620,732
[57] McCoubrey, A. and Mathieson, D. W., *J. chem. Soc.*, **1949**, 696
[58] *Bull. Soc. Path. exot.*, 1948, **41**, 464
[59] Berg, S. S. and Newbery, G., *J. chem. Soc.*, **1949**, 642
[60] Hewitt, R. I., Gumble, A., Kushner, S., Safir, S. R., Brancone, L. M., Subbarow, Y., *J. Pharmacol.*, 1949, **96**, 305
[61] *J. Pharm. Pharmacol.*, 1949, **1**, 11
[62] U.S.P. 2,463,861; *Ann. trop. Med. Parasit.*, 1949, **42**, 357
[63] Williamson, J. and Lourie, E. M., *Nature*, 1948, **161**, 103
[64] Friedheim, E. A., *Amer. J. trop. Med.*, 1949, **29**, 173
[65] B.P. 618,039
[66] Marsh, D. F. and Woodbury, R. A., *J. Amer. chem. Soc.*, 1949, **71**, 3748
[67] Fox, H. H. and Wenner, W., U.S.P. 2,465,307–8; McGeachin, R. L., *J. Amer. chem. Soc.*, 1949, **71**, 3755
[68] *J. Parasitol.*, 1949, **35**, 375

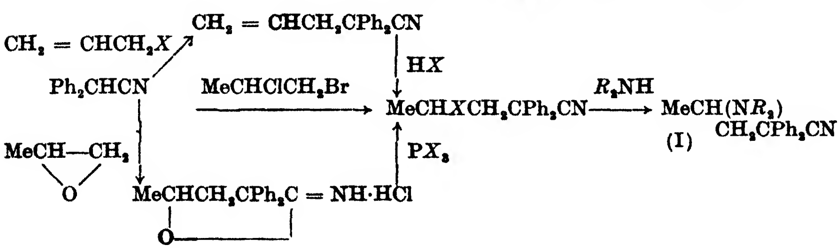
AMIDONE AND RELATED ANALGESICS (J. Elks, Ph.D., F.R.I.C.)

SINCE this subject was last reviewed in these Reports (1947) a large number of papers have appeared, both on the pharmacological and clinical applications of amidone itself and on the preparation and properties of analogous compounds.

E. M. Schultz and J. M. Sprague[1] have further studied the reaction leading to the isomeric cyanides [(I); R = Me] and [(III); R = Me], intermediates in the preparation of amidone [(II); R = Me, R' = Et] and *iso*amidone [(IV); R = Me, R' = Et] respectively. They found that 2-chloro-1-dimethylaminopropane and 1-chloro-2-dimethylaminopropane could be prepared in the pure state from the corresponding alcohols and that each of these compounds reacted with diphenylmethyl cyanide to yield a mixture of roughly equal parts of [(I); R = Me] and [(III); R = Me]. Although 1-chloro-2-dimethylaminopropane could be isomerized to the secondary halide by heating, either as the base[2] or the hydrochloride, 2-chloro-1-dimethylaminopropane was quite stable. Hence the conclusion was drawn that, in the usual synthesis of amidone from the secondary chloride, rearrangement—probably through an ethylene-iminium salt—occurs during the reaction with diphenylmethyl cyanide and not, as suggested by W. R. Brode and M. W. Hill,[3] during the preparation of the chloroamine from the amino-alcohol.



This type of rearrangement, which has been encountered repeatedly when an unsymmetrically substituted chloroethylamine derivative reacts with a diarylmethyl cyanide, is inconvenient in practice, since it produces much unwanted isomer which, in some cases, is not easy to separate. Some alternative routes to amidone and its analogues have been investigated by J. Attenburrow *et al.*[2] and by N. R. Easton, J. H. Gardner and J. R. Stevens[4] with a view to eliminating this difficulty. These proceed *via* 3-halogeno-1 : 1-diphenylbutyl cyanides prepared by addition of hydrogen bromide or hydrogen iodide to 1 : 1-diphenylbut-3-enyl cyanide,[2] by treatment of diphenylmethyl cyanide with 2-chloro-1-bromopropane,[2] or by the action of phosphorus halides upon 2-imino-3 : 3-diphenyl-5-methyltetrahydrofuran hydrochloride[4]; the free base corresponding to this last compound results from the action of propylene oxide upon diphenylmethyl cyanide in the presence of sodamide.[2,4] Treatment of the halogeno-cyanides with dimethylamine or morpholine gives the required amino-cyanides [(I); R = Me or R_2 = $-[CH_2]_2O[CH_2]_2-$], but in very poor yield, the main reaction being a dehydrohalogenation.[2,4]



An improvement in the original method of preparation of amidone has recently been described by J. W. Cusic,[5] who used sodium hydroxide in the reaction between 2-chloro-1-dimethylaminopropane and diphenylmethyl cyanide, thus avoiding the use of sodamide, lithium amide or potassium *tert.*-butoxide. This method, which gave a very satisfactory yield, should be applicable to similar reactions.

Recent patents describe the preparation, in high yield, of diphenylmethyl cyanide from benzaldehyde cyanohydrin and benzene in the presence of either aluminium chloride[6] or boron trifluoride.[7]

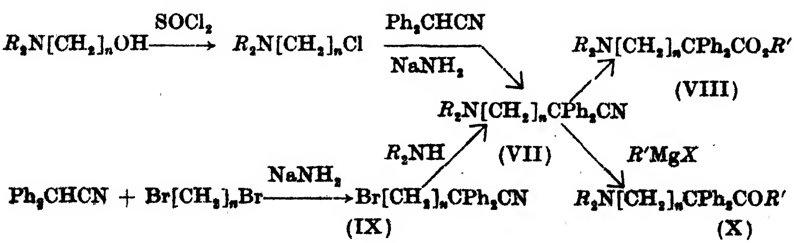
Several methods have been published for the resolution of amidone, itself, rather than the intermediate 3-dimethylamino-1 : 1-diphenylbutyl cyanide. W. R. Brode and M. W. Hill,[8] and A. A. Larsen, B. F. Tullar, B. Elpern and J. S. Buck[9] employed D-tartaric acid for the resolution, while E. E. Howe and M. Sletzinger[10] found that the pure optically active forms were very readily obtained, in high yield, from the (+)-α-bromocamphor-π-sulphonate of DL-amidone.

*iso*Amidone, 6-dimethylamino-4 : 4-diphenyl-5-methylhexan-3-one [(IV) ; R = Me, R' = Et] prepared from 3-dimethylamino-1 : 1-diphenyl-*iso*butyl cyanide [(III) ; R = Me] by treatment with an ethylmagnesium halide and vigorous acid hydrolysis of the rather stable ketimine so formed,[11] has been given considerable pharmacological and clinical study[12–17] and appears promising, having only slightly less analgesic effect than amidone, with rather lower toxicity and decreased tendency to cause side-effects and to give rise to tolerance. The (+) and (−) forms of *iso*amidone have been prepared by resolution of the intermediate cyanide [(III) ; R = Me] by means of D-tartaric acid followed by conversion to the ketone,[9] or by resolution of the ketone itself, either as its D-tartrate[9] or by way of its salt with *p*-nitrobenzoyl-L-glutamic acid, a reagent which has not previously been used for resolution.[10] The activity of *iso*amidone has been found to be very largely contributed by the (−) form.[18]

A number of analogues [(V) and (VI) ; R'' = alkyl] of amidone and *iso*amidone have been prepared by reaction of 2-chloro-1-dialkylamino-alkanes with diarylmethyl cyanides, separation of the mixture of amino-cyanides and treatment of each with a Grignard reagent. M. E. Speeter, W. M. Byrd, L. C. Cheney and S. B. Binkley[19] have taken advantage of the greater stability of the branched chain ketimines by treating the mixed amino-cyanides with the Grignard reagent, decomposing the complex with hydrochloric acid and separating the ketone [(V) ; R_2 = $-[CH_2]_2O[CH_2]_2-$, R' = Et, R'' = Me] from the ketimine corresponding to [(VI) ; R_2 = $-[CH_2]_2O[CH_2]_2-$, R' = Et, R'' = Me] ; the latter compound was then converted to the ketone by vigorous acid hydrolysis.

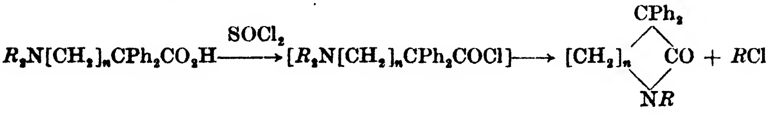
$R''CH(NR_2)CH_2CPh_2COR'$	$R_2NCH_2CHR''CPh_2COR'$
(V)	(VI)

Some straight-chain esters (VIII) and ketones (X) with terminal basic groups have been described by M. Bockmühl and G. Ehrhart,[20] and by D. J. Dupré, J. Elks, B. A. Hems, K. N. Speyer and R. M. Evans.[21] The intermediate cyanides (VII) were prepared either by reaction of di-alkylaminoalkyl chlorides with diphenylmethyl cyanide in the presence of sodamide, or by the reaction of diphenylmethyl cyanide with an



alkylene dibromide, and treatment of the resulting ω-bromodiphenylalkyl cyanide (IX) with a secondary amine (as shown on p. 332).

The cyanides were converted to ketones by treatment with Grignard reagents, and to esters either directly by alcoholysis,[21] or by hydrolysis to the acid, followed by esterification.[22] Attempts to convert the carboxylic acids [(VIII); $n = 2$, $R =$ Me or Et, $R' =$ H] to the esters *via* the acid chlorides were unsuccessful, the chlorides cyclizing to pyrrolidones.[21] The homologous acid chloride derived from [(VIII); $n = 3$, $R =$ Et, $R' =$ H] was more stable and could be converted to the ethyl ester, but closer study of this reaction[23] has shown that more vigorous conditions will cause cyclization of such 4-dialkylaminobutane-1-carboxyl chlorides also, to yield piperidones.



An alternative method of preparation of the esters (VIII) involved the reaction of the appropriate chloroalkylamine with the sodio-derivative of diphenylacetic ester, which was prepared from diphenylacetic ester by reaction with sodio-diethylmethyl cyanide.[20]

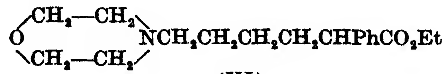
A number of esters, both of types [(VIII); $n = 0 - 3$] and [(V); $R'' =$ Me, $R' =$ OAlk] have been prepared and tested for analgesic activity.[19–22]. Activity was greatest in the lower alkyl esters but, in general, was smaller than that of the corresponding ethyl ketones; the variation in activity due to other changes in the molecule paralleled that found in the ketones (*see below*).

Among the ketones (V), (VI) and (X) in which R' has been varied, maximum activity among the alkyl ketones was found when $R' =$ Et.[20–22] Aryl and aralkyl ketones had low activity but the one allyl ketone reported [(X); $n = 2$; $R_2 = -[CH_2]_5-$; $R' = CH_2CH = CH_2$] was almost as active as the corresponding ethyl ketone.[20]

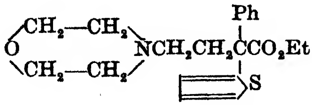
The nature of the basic group has been shown to be of great importance. In the series of compounds [(V); $R' =$ Et, $R'' =$ Me] and [(X); $n = 2$, $R' =$ Et] the dimethylamino compounds were the most active among the non-cyclic compounds, but cyclic amino groups ($R_2 = -[CH_2]_4-$, $-[CH_2]_5-$, or $-[CH_2]_2O\ [CH_2]_2-$) conferred rather high activity, the morpholino-compounds [(V); $R_2 = -\ [CH_2]_2O\ [CH_2]_2-$, $R' =$ Et, $R'' =$ Me] and [X; $n = 2$, $R_2 = -[CH_2]_2O\ [CH_2]_2-$, $R' =$ Et] being particularly active.[2,19,20,21,24] The first of these compounds, i.e. 4 : 4-diphenyl-6-morpholinoheptan-3-one has been marketed under the name of 'Heptalgin': tests have shown that the activity of this compound is similar to that of amidone, but that its toxicity is much lower; side-effects seem to be unimportant but the analgesic effect is rather more short-lived than that of amidone.[15,25,26,27] Preliminary reports on the piperidine analogues [(V) and (VI); $R_2 = -[CH_2]_5-$; $R' =$ Et, $R'' =$ Me] of amidone and *iso*amidone indicate that these may have useful properties.[24]

The length of the chain in esters and ketones (VIII) and (X) has been shown to be critical, activity being found only in those with $n = 2$, although compounds have been prepared with n ranging from 0 to 4.[20,21]

However, R. M. Anker and A. H. Cook[28] have reported that 1-phenyl-5-morpholinopentan-1-carboxylic ester (XI) has about one-third the activity of pethidine.



(XI)



(XII)

Compounds related to [(V); $R'' =$ Me], [(VIII); $n = 2$] and [(X); $n = 2$], but with the phenyl groups bearing substituents (Cl, Br, OH, OMe, Me),[20,21,29,30] with the benzene rings as part of a fluorene system,[20,29,31] and with one or both phenyl rings replaced by alkyl, aralkyl or heterocyclic groups[20,29,30,32] have been tested and found in almost every case to have little or no activity. The thiophen compound (XII) was an exception, having some four times the analgesic activity of pethidine.[32]

Compounds of type [(V); $R'' =$ Me] were always notably more active than their lower homologues [(V); $R'' =$ H] but a compound [(V); $R =$ Me, $R' = R'' =$ Et] with a still longer chain was quite inactive.[20] Comparison of results on isomeric compounds in the amidone series [(V); $R'' =$ Me] and *iso*amidone series [(VI); $R'' =$ Me] has shown that the analogues of *iso*amidone are, in general, less active than those of amidone, sometimes considerably so.[2,19,20,24]

A few amides of types [(V); $R' = NH_2$] and [(X); $R' = NH_2$] have been prepared and found inactive.[20,22] Quite high activity was found in the aldehyde [(X); $n = 2$, $R_2 = -[CH_2]_5-R' =$ H] which was prepared from the acid [(VIII); $n = 2$, $R_2 = -[CH_2]_5-$, $R' =$ H] by conversion to its chloride and hydrogenation in the presence of a palladium catalyst.[20] M. Bockmühl and G. Ehrhart[20] found that the carbinol obtained by catalytic reduction of [(X); $n = 2$, $R_2 = -[CH_2\cdot]_5-$, $R' =$ Me] was inactive, but more recent work has shown that esters of such carbinols have quite high activity.

$$R''CH(NR_2)CH_2CPh_2CH(OR')Et$$

(XIII)

$$R_2NCH_2CHR''CPh_2CH(OR')Et$$

(XIV)

E. L. May and E. Mosettig[33] found that both amidone and *iso*amidone could be reduced to the corresponding carbinols [(XIII); $R = R'' =$ Me, $R' =$ H)] and [(XIV); $R = R'' =$ Me, $R' =$ H] respectively, by means of lithium aluminium hydride, though *iso*amidone, unlike its isomer, was resistant to catalytic hydrogenation. This difference in behaviour, which is presumably due to the presence of a methyl group β to the carbonyl group in *iso*amidone, recalls the greater stability of the ketimines derived from this compound and its analogues, as compared with the

straight-chain compounds. Although compounds of types [(XIII); R'' = Me] and [(XIV); R'' = Me] possess two asymmetric carbon atoms there has been no report of the isolation of diastereoisomeric forms after reduction of the corresponding ketones. The carbinols were converted into esters of various types and a wide range of such esters has been prepared by similar methods.[19,34,35]

Although the carbinols had little or no activity, the corresponding acetates [(XIII) and (XIV); R' = Ac] were about as active as the original ketones,[19,33,34,35] other esters being rather less effective. In particular, very high activity: toxicity ratios have been claimed for the morpholino compounds [(XIII); $R_2 = -[CH_2]_2O[CH_2]_2-$, R' = Ac, R'' = H or Me].[19] According to T. R. Sherrod *et al.*[36] these compounds are of interest, on account of high activity: toxicity ratios and of prolonged action.

L. C. Cheney, R. R. Smith and S. B. Binkley[37] and N. R. Easton *et al.*[11] have isolated a number of ketimines [(XV); R' = H, R'' = H or Me and (XVI); R' = H, R'' = Me] the less stable straight-chain compounds being prepared by decomposition of the Grignard complexes under mild conditions. The acyl derivatives were prepared by treatment either of the imines or of the intermediate Grignard complexes [(XV) and (XVI); R' = MgX] with the appropriate acid chloride. The imines had a more favourable activity: toxicity ratio than the corresponding ketones, and the acyl compounds were better still in this respect.

$$R''CH(NR_2)CH_2CPh_2C(:NR')Et$$
(XV)

$$R_2NCH_2CHR''CPh_2C(:NR')Et$$
(XVI)

$$R_2NCH_2CH_2CPh_2OR'$$
(XVII)

The sulphone analogues of amidone and some of the other analgesic ketones have been prepared by reaction of benzhydryl ethyl sulphone with the appropriate chloroalkylamine.[38] These sulphones had very high activity with comparatively low acute toxicity,[38,39] but the sulphone analogue of amidone itself has been shown to have the disadvantage that tolerance to the drug develops particularly rapidly.[14]

F. Bergel and A. L. Morrison[40] in an extensive review of synthetic analgesics refer to a private communication to the effect that esters [(XVII); R' = acyl] of 3-dialkylamino-1 : 1-diphenylpropanols [(XVII); R' = H] are inactive, in spite of their formal resemblance to the highly active 4-acyloxy-4-phenyl-1-methylpiperidines.

References

[1] *J. Amer. chem. Soc.*, 1948, **70**, 48
[2] Attenburrow, J., Elks, J., Hems, B. A. and Speyer, K. N., *J. chem. Soc.*, **1949**, 510
[3] *J. Amer. chem. Soc.*, 1947, **69**, 724
[4] Ibid., 1947, **69**, 2941
[5] Ibid., 1949, **71**, 3546

[6] Homeyer, A. H. and Splitter, J. S., U.S.P. 2,443,246
[7] Mills, J., U.S.P. 2,447,419
[8] *J. org. Chem.*, 1948, **13**, 191
[9] *J. Amer. chem. Soc.*, 1948, **70**, 4194
[10] Ibid., 1949, **71**, 2935
[11] Easton, N. R., Gardner, J. H., Evanick, M. L. and Stevens, J. R., ibid., 1948, **70**, 76
[12] Gentling, A. A. and Lundy, J. S., *Proc. Mayo Clinic*, 1947, **22**, 249
[13] Isbell, H. and Eisenman, A. J., *J. Pharm. exp. Ther.*, 1948, **93**, 305
[14] Lewis, J. R., ibid., 1949, **96**, 31
[15] Flataker, L. and Winter, C. A., *Fed. Proc.*, 1949, **8**, 47
[16] Hoppe, J. O. and Miller, L. C., ibid., 1948, **7**, 228
[17] Denton, J. E., Straus, O. H., Waddell, W. E. and Beecher, H. K., ibid., 1948, **7**, 214
[18] Jenney, E. H. and Pfeiffer, C. C., ibid., 1948, **7**, 231
[19] *J. Amer. chem. Soc.*, 1949, **71**, 57
[20] *Ann. Chem.*, 1948, **561**, 52
[21] *J. chem. Soc.*, **1949**, 500
[22] Walton, E., Ofner, P. and Thorp, R. H., ibid., 648
[23] Clarke, R. L., Mooradian, A., Lucas, P. and Slauson, T. J., *J. Amer. chem. Soc.*, 1949, **71**, 2821
[24] Ofner, P., Thorp, R. H. and Walton, E., *Nature*, 1949, **163**, 479
[25] Wilson, W. M. and Hunter, R. B., *Brit. med. J.*, 1948, ii, 553
[26] Hewer, A. J. H. and Keele, C. A., *Lancet*, 1948, **255**, 683
[27] Hewer, A. J. H., Keele, C. A., Keele, K. D. and Nathan, P. W., ibid., 1949, **256**, 431
[28] *J. chem. Soc.*, **1948**, 806
[29] Shapiro, D., *J. org. Chem.*, 1949, **14**, 839
[30] Weiss, P., Cordasco, M. G. and Reiner, L., *J. Amer. chem. Soc.*, 1949, **71**, 2650
[31] Ginsburg, O. and Baizer, M. M., ibid., 1500
[32] Brown, D. J., Cook, A. H. and Heilbron, I. M., *J. chem. Soc.*, **1949**, S.111, S.113
[33] *J. org. Chem.*, 1948, **13**, 663
[34] Pohland, A., Marshall, F. J. and Carney, T. P., *J. Amer. chem. Soc.*, 1949, **71**, 460
[35] May, E. L. and Mosettig, E., *J. org. Chem.*, 1948, **13**, 459
[36] Sherrod, T. R., Kaiser, R., Santos-Martinez, J. and Pfeiffer, C. C., *Fed. Prod.*, 1948, **7**, 255
[37] *J. Amer. chem. Soc.*, 1949, **71**, 53
[38] Klenk, M. M., Suter, C. M. and Archer, S., ibid., 1948, **70**, 3846
[39] Tullar, B. F., Wetterau, W. and Archer, S., ibid., 3959
[40] Bergel, F. and Morrison, A. L., *Quart. Rev. chem. Soc.*, 1948, **2**, 349

VITAMINS (A. W. D. Avison, B.Sc., F.R.I.C.)

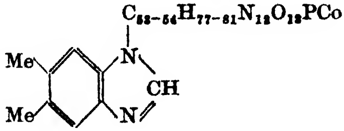
Roche Products Limited

Within the confines set here it is possible only to mention briefly some of the more striking advances made during the period under review, the subject being now so vast that many volumes might be required to give a complete account of present knowledge.

B Vitamins

Anti-pernicious-anaemia factor, Vitamin B_{12}.—The red crystalline B_{12} isolated from liver by workers in America[1] and Britain[2,3,4] has been shown to be produced also by a mould, *Streptomyces aureofaciens.*[5] The compound is optically active and elementary analysis and molecular weight determination[6] together with hydrolytic degradation[7,7a] show it to be a 5 : 6-dimethylbenziminazole derivative of the type shown (I). The

presence of cobalt[8] was not altogether surprising in view of the previous implication of this element in haematopoiesis. Rather surprisingly for such a large molecule, there are no peptide linkages.[6] The use of vitamin B_{12} in medicine has been discussed with reference to its influence on the metabolism of thymidine[9] and its relation to other active substances.[9,10] The vitamin may be assayed microbiologically, since *inter alia* it is an



(I)

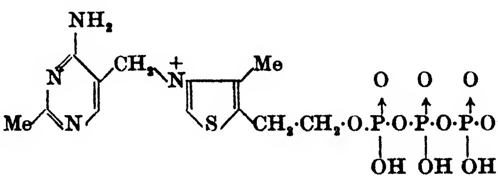
essential growth factor for *Lactobacillus leichmanii*.[11] The early recognition of the existence of a second clinically active substance in liver[2] has been followed by its isolation from *Streptomyces aureofaciens*[12] and the demonstration of its activity both in the chick assay and the *L. leichmannii* test. This is termed vitamin B_{12a} to distinguish it from vitamin B_{12b}, the hydrogenated vitamin, which is also active.[13]

Vitamin B_{12} in addition to its haematopoietic effect may be involved in the utilization of protein by mammals.[14]

Riboflavin.—The recent patent literature discloses a great deal of interest in the production of riboflavin by fermentation using the mould, *Eremothecium ashbyii*[15–20] or the bacterium, *Clostridium acetobutylicum*.[21,22] The development of deep-culture techniques and the high vitamin concentrations realized make this an attractive method of riboflavin preparation which may rival its chemical synthesis.

Aneurin.—The pyrophosphate ester of aneurin (cocarboxylase) has recently been demonstrated to be of great value in the treatment of diabetic coma.[23]

Phosphorylation of aneurin with the crude trimetaphosphoric acid obtained by pyrolysis of orthophosphoric acid is claimed to give in excellent yield the triphosphoric acid ester (II).[24,25] Like the analogous



(II)

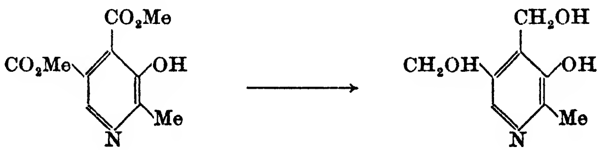
adenosine-5′-triphosphate (ATP), this ester has been found to have interesting actions on the heart.[26,27] It has also about 80% of the co-enzyme activity of cocarboxylase.[28]

Partially hydrolysed phosphoryl chloride phosphorylates aneurin to give mixtures containing polyphosphates in which some of the phosphate groups are attached to the pyrimidine amino group.[29] Such compounds appear to be devoid of cocarboxylase activity.[30]

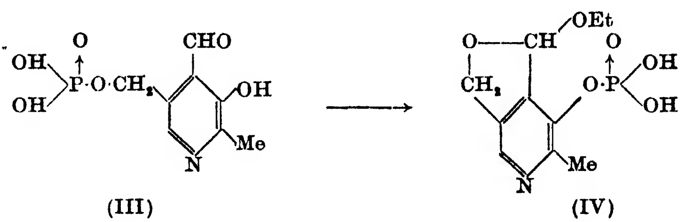
Pantothenic acid (*Coenzyme A*), important in biological acetylating systems, contains pantothenic acid which is not available in the *Lactobacillus* test until after treatment with intestinal phosphatase + pigeon liver extract. Since phosphomonoesterases also fail to liberate the pantothenic acid in these experiments it is concluded that the coenzyme contains a phosphate bridge from pantothenic acid to a second constituent.[31–33]

Biotin.—Biotin has been implicated in oxalacetate decarboxylase and serine, threonine and aspartic acid deaminase systems. The coenzyme is present in yeast extract[34] and reactivation of the apoenzyme of aspartic acid deaminase also occurs with biotin + adenosine-5′-phosphoric acid, neither alone having any effect. Isolation of a pure active compound, for which the name *biocytin* is proposed, was announced in a communication[35] to the 1st International Congress of Biochemistry, but unfortunately no printed publication of this or later work has so far appeared.

Pyridoxin.—A greatly simplified synthesis of pyridoxin has recently been described[36] involving lithium aluminium hydride reduction of dimethyl 3-hydroxy-2-methylpyridine-4 : 5-dicarboxylate[37] :



The structure of pyridoxal phosphate, active as L-tyrosine codecarboxylase and in other systems, has been demonstrated fairly conclusively to be (III) and not the 3-phosphate. The latter, prepared as its ethyl acetal (IV) by Swiss workers and claimed by them[38] to be the



(III) (IV)

coenzyme, has recently been shown[39] to have only a fraction of the biological activity of a phosphorylated pyridoxal of non-specified structure obtained by the action of $POCl_3$ on pyridoxal and fractionation of barium salts. Unequivocal synthesis of (III) would thus be of great interest in this field.

The shift of attention from what we normally accept as vitamins to their derivatives active in metabolic processes is now very marked. The well-known phenomenon of producing vitamin deficiencies by the administration of massive doses of the same or a different vitamin receives an explanation[40–42] in terms of the exhaustion of e.g. phosphorylating mechanisms of the body during assimilation and excretion. Thus, a

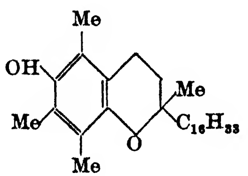
definite challenge is presented to the manufacturer to produce not only that fragment fortuitously isolated and called 'vitamin,' but an appropriate phosphorylated form especially where large and prolonged doses may be required.

Vitamin *C*

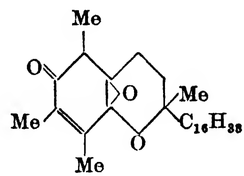
A very recent use of ascorbic acid in medicine is worth recording. It has been found that in rheumatoid arthritis the dramatic cures achieved with Cortisone can in many cases be duplicated with desoxycorticosterone acetate (DOCA) when a massive intravenous injection of ascorbic acid is given simultaneously.[43] In spite of some negative evidence[44] there has been sufficient confirmation[45–48] of this result to make it of paramount interest. The DOCA may be replaced by testosterone or progesterone.[49]

Vitamin *E*

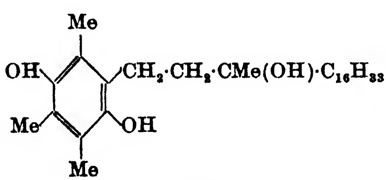
The chemical nature of vitamin-*E*-active substances has been much clarified by recent work. It has been demonstrated that in the standard rat bioassay D-α-tocopheryl acetate is 36% more potent than the DL-α-tocopheryl acetate used as international standard.[50,51] A biologically active primary oxidation product of α-tocopherol (V) isomeric with the inactive α-tocopheryl quinone has been isolated[52] for which an epoxide structure (VI) is suggested arising *via* a semiquinone intermediate.



(V)



(VI)



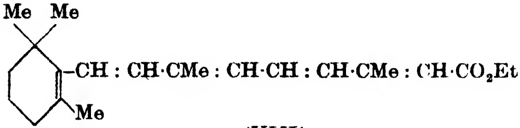
(VII)

Studies on creatine excretion by patients with progressive muscular dystrophy and by dystrophic rabbits have shown that in this condition α-tocopheryl hydroquinone (VII) is the active compound rather than α-tocopherol. The triacetate, diacetate and diphosphate of (VII) are without effect.[53]

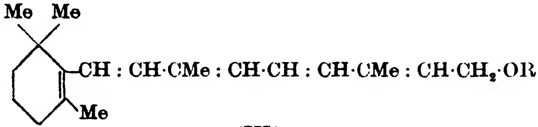
Recent work[52] has shown that many substances previously believed to have vitamin *E* activity are, in fact, inactive and the structure requirements for this type of activity are therefore more specific than was thought hitherto.

Vitamin *A*

In the Pedler Lecture for 1947[54] it was suggested that lithium aluminium hydride reduction of esters of vitamin *A* acid ought to give vitamin *A* [(IX); *R* = H]. This has now been realized in the case of the ethyl ester (VIII), a 95% yield of a product of 95% purity being obtained.[55,55a]



(VIII)

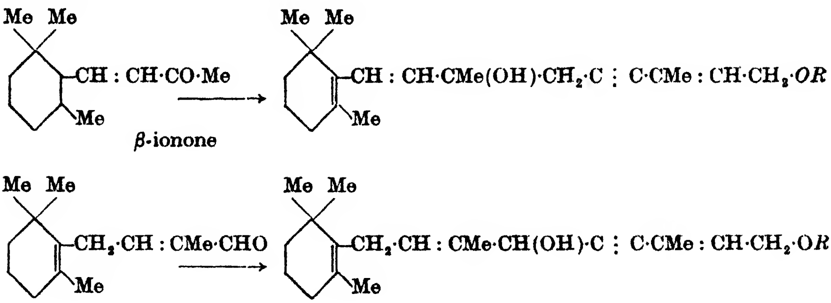


(IX)

Further details of the various syntheses of vitamin *A* and its derivatives by the Swiss group are now available in the patent literature.[56–59] These include variations on the original Grignard reaction with

CH⋮C·CMe:CH·CH$_2$·O*R*

on the aldehyde (X) obtained by glycide ester synthesis with β-ionone,[60] as well as Reformatsky- or Grignard-type reactions with a substituted propargyl bromide, CH$_2$Br·C⋮C·CMe:CH·CH$_2$·O*R*, on β-ionone itself:



(X)

Appropriate sequences of partial reduction, allyl rearrangement and dehydration or dehydrohalogenation then follow. The same workers have recently described[61] the preparation in a pure state of synthetic vitamin *A* acetate, succinate, butyrate, laurate, palmitate, stearate, oleate and benzoate as well as the methyl and phenyl ethers, several in a crystalline form.

References

1 Rickes, E. L., Brink, N. G., Koniuszy, F. R., Wood, T. R. and Folkers, K., *Science*, 1948, **107**, 396

2 Smith, E. L., *Nature*, 1948, **161**, 638

[3] Smith, E. L. and Parker, L. F. J., *Biochem. J.*, 1948, **43**, Proc. viii
[4] Ellis, B., Petrow, V. and Snook, G. F., *J. Pharm. Pharmacol.*, 1949, **1**, 60
[5] Duggar, B. M., *Annals N.Y. Acad. Sci.*, 1948, **51**, 175
[6] Brink, N. G., Wolf, D. E., Kaczka, E., Rickes, E. L., Koniuszy, F. R., Wood, T. R. and Folkers, K., *J. Amer. chem. Soc.*, 1949, **71**, 1854
[7] Brink, N. G. and Folkers, K., ibid., 295
[7a] Holiday, E. R. and Petrow, V. *et al.*, *J. Pharm. Pharmacol.*, 1949, **1**, 957
[8] Smith, E. L., *Nature*, 1948, **162**, 144
[9] West, R. and Reisner, E. H., 1st International Congress of Biochemistry, 1949, Abstracts of Communications, p. 70
[10] Ungley, C. C., *ibid.*, p. 76
[11] Hoffmann, C. E., Stockstad, E. L. R., Hutchings, B. L., Dornbush, A. C. and Jukes, T. H., *J. biol. Chem.*, 1949, **181**, 635
[12] Pierce, J. V., Page, A. C., Stockstad, E. L. R. and Jukes, T. H., *J. Amer. chem. Soc.*, 1949, **71**, 2952
[13] Kaczka, E., Wolf, D. E. and Folkers, K., ibid., 1514
[14] Hartman, A. M., Dryden, L. P. and Cary, C. A., *Arch. Biochem.*, 1949, **23**, 165
[15] Merck, B.P. 593,027, 621,401
[16] Pfizer, B.P. 593,953
[17] Rhône Poulenc, B.P. 594,015
[18] Glaxo Ltd., B.P. 607, 008
[19] Roche Products, B.P. 615,847
[20] Commercial Solvents, B.P. 623,082
[21] Commercial Solvents, B.P. 553,465, 553,903, 553,904, 621,468, 621,469, 621,552
[22] Western Condensing Co., B.P. 602,029, 602,031
[23] Markees, S. and Meyer, F. W., *Schweiz. med. Wochenschr.*, 1949, 931
[24] Viscontini, M., Bonnetti, G. and Karrer, P., *Helv. chim. Acta*, 1949, **32**, 1478
[25] Velluz, L., Amiard, G. and Bartos, J., *C.R. Acad. Sci., Paris*, 1948, **226**, 735
[26] Velluz, L., Jequier, R. and Plotka, C., ibid., 1855
[27] Plotka, C., Peterfalvi, M., Jequier, R. and Velluz, L., *Amer. J. Physiol.*, 1949, **158**, 279
[28] Velluz, L., Amiard, G. and Bartos, J., *J. biol. Chem.*, 1949, **180**, 1137
[29] Roux, H., Teysseire, Y. and Duchesne, G., *C.R. Soc. Biol., Paris*, 1948, **142**, 368
[30] Roux, H., Teysseire, Y. and Richer, G., ibid., **143**, 524
[31] Kaplan, N. O. and Lipmann, F., *J. biol. Chem.*, 1948, **174**, 37
[32] Hegsted, D. M. and Lipmann, F., ibid., 89
[33] Lipmann, F., 1st International Congress of Biochemistry, 1949, Abstracts of Communications, p. 230
[34] Ibid., p. 325
[35] Wright, L. D., Cresson, E. L., Skeggs, H. R., Wood, T. R., Peck, R. L., Wolf, D. E. and Folkers, K., 1st International Congress of Biochemistry, 1949, paper read but not published
[36] B.P. 629, 450
[37] Cohen, A., Barell Jubilee Volume, 1946, p. 71; B.P. 556,044
[38] Karrer, P., Viscontini, M. and Forster, O., *Helv. chim. Acta*, 1948, **31**, 1004
[39] Umbreit, W. W. and Gunsalus, I. G., *J. biol. Chem.*, 1949, **179**, 279
[40] Magyar, I., *Experientia*, 1948, **4**, 33
[41] Magyar, I., Gábor and Eöllös, Z., *Acta med. scand.*, 1949, **135**, 142
[42] Magyar, I. and Gábor, G., *Int. Rev. Vitamin Res.*, 1949, **21**, 1
[43] Lewin, E. and Wassén, E., *Lancet*, 1949, **257**, 993
[44] Kellgren, J. H., ibid., 1204
[45] Loxton, G. E. and Le Vay, D., ibid., 1204
[46] Robertson, J. A., *Lancet*, 1950, **258**, 134
[47] Nashat, F., ibid., 135
[48] Fox, W. W., ibid., 135
[49] Landsberg, M., ibid., 134
[50] Harris, P. L., *Ann. N.Y. Acad. Sci.*, 1949, **52**, 342
[51] Harris, P. L. and Ludwig, M. I., *J. biol. Chem.*, 1949, **179**, 1111
[52] Boyer, P. D., Rabinovitz, M. and Liebe, E., *Ann. N.Y. Acad. Sci.*, 1949, **52**, 188
[53] Milhorat, A. T., Mackenzie, J. B., Ulick, S., Rosenkrantz, H. and Bartels, W. E., ibid., 334
[54] Heilbron, (Sir) I., *J. chem. Soc.*, **1948**, 390

[55] Schwarzkopf, O., Cahnmann, H. J., Lewis, A. D., Swidinsky, J. and Wuest, H. M., *Helv. chim. Acta*, 1949, **32**, 44
[55a] B.P. 633,749
[56] Isler, O. and Businger, A., U.S.P. 2,475,139
[57] Isler, O., U.S.P. 2,451,739, 2,451,738, 2,451,737, 2,451,736, 2,451,735
[58] B.P. 626,392, 624,486, 623,826, 622,510, 619,898, 605,772, 605,208
[59] Huber, W., U.S.P. 2,451,741
[60] Lindlar, H., U.S.P. 2,451,742, 2,451,740
[61] Isler, O., Ronco, A., Guex, W., Hindley, N. C., Huber, W., Dialer, K. and Kofler, M., *Helv. chim. Acta*, 1949, **32**, 489

AMIDINES (P. Oxley, M.A., B.Sc.)

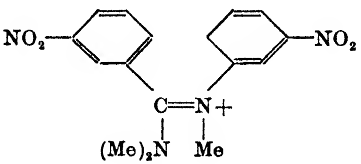
Boots Pure Drug Co., Ltd.

THE bactericidal and trypanocidal activity of the aromatic diamidines was discovered almost a decade ago (for references, *see* Yorke[1], Heathcote[2]) and the use of these compounds for the prophylaxis and treatment of a number of protozoal infections is now well established[3] although their precise mode of action still remains to be discovered.[4–6] Stilbamidine has also been used with partial success in the treatment of multiple myeloma.[7] The effect of modifications in the structure of these diamidines has been investigated by the May and Baker research team, whose recent papers record the preparation of nuclear substituted derivatives of stilbamidine[8,9] and of the diamidinodiphenoxyalkanes.[10] It was found that hydroxyl and halogen substituents *meta* to the amidine groups increased the trypanocidal but not the bactericidal activity of stilbamidine, whereas in the diamidinodiphenoxyalkane series the reverse was true.[11,12] Iodohexamidine and dibromopropamidine may have some application as local antiseptics,[13–15] but are apparently unsatisfactory for the treatment of systemic bacterial infections.[16] Activity against influenza virus *in vitro* has been found in certain aromatic diamidines.[16a] Replacement of the benzene nuclei of the aromatic diamidines by other ring systems[17–19] has been found to increase the toxicity. It has been known for some time that the toxicity of stilbamidine solutions increased on exposure to sunlight, owing to the formation of a dimer which has now been isolated and characterized.[20]

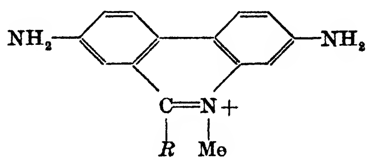
Following the discovery of activity in the diamidines, many different types of monoamidines have been examined. *p*-Sulphonamidobenzamidine and the corresponding amidoxime were rickettsiostatic in laboratory animals,[21,22] but did not modify the clinical course of typhus; and *p*-methylsulphonylbenzamidine showed highly specific activity against the causative organisms of tetanus and gas gangrene.[23,24] Any modification of the structure of these compounds virtually abolished their activity,[25,26] and no outstanding antibacterial activity has been found in other simple aromatic or heterocyclic amidines,[27–31] although condensed amidine and guanidine residues figure prominently in the structure of such compounds as Paludrine and Antrycide, and the most active aminoacridines are those which incorporate amidine vinylogues.

A number of higher aliphatic amidines[32] and several different types of *N*-aryl mono- and diamidines[33] have recently been shown to possess very high *in vitro* activity against *M. tuberculosis*, but no activity could be demonstrated *in vivo*. The highly specific activity of the *N*-arylamidines against mycobacteria is rather surprising, for *N*-substituted amidines in general seem to be almost devoid of antibacterial activity.

Quaternary amidinium salts such as (I), prepared by condensation of *m*-nitrobenzdimethylamide with *m*-nitromethylaniline in presence of phosphorus oxychloride, had little or no trypanocidal activity[34] in spite of their formal resemblance to the highly active phenanthridinium compounds (II). It is interesting to note in this connexion that a new synthesis of phenanthridines by cyclization of *N*-diphenylylamidines has recently been reported.[35]



(I)



(II)

Synthesis

Many of the amidines recorded in the literature have been prepared by Pinner's iminoether method, two interesting extensions of which have recently been reported. α-Aminocarbonyl compounds have been shown to react with iminoether hydrochlorides to give iminazoles,[36,37] and 5-alkoxyacridines (which may be considered as iminoether vinylogues) react very readily with ammonium salts, yielding 5-aminoacridines.[38] A modification of Pinner's method involves reaction of the free iminoether with an aqueous solution of an ammonium salt, and has the dual advantages of greater convenience on the large scale and direct production of salts other than halides.[39] This is important in the case of the aromatic diamidines which form sparingly soluble hydrochlorides and are normally used as the more soluble isethionates. However, the method still suffers from the basic disadvantage that most *ortho*-substituted and other sterically hindered cyanides will not give iminoethers.

Since the subject of amidine chemistry was last reviewed,[40] several new methods of synthesis have been evolved. The first of these depends on the observation that when a cyanide is heated with an ammonium arylsulphonate an equilibrium mixture containing the amidinium salt is produced.[41,42] The reaction is not hindered by *ortho* substituents, and fairly good yields of unsubstituted and *N*-alkylamidines are obtained at about 250° C. Arylamine salts react more readily and give very high yields of *N*-arylamidines at 180–200° C. Unsubstituted amidines are also obtained from cyanides and ammonium thiocyanate at 180° C. but this reaction fails with *ortho*-substituted cyanides and probably involves addition of ammonia rather than the ammonium ion to the cyano group.[43]

It has been shown that amidines are formed by the direct addition of ammonia and alkylamines to cyanides, although the more feebly basic

arylamines do not react.[44] The temperature at which this addition will take place depends on the degree of polarization of the cyano group, which is enhanced by the presence of electron-attracting substituents in the molecule. Catalysts of the Friedel–Crafts type, such as aluminium chloride, form addition compounds with cyanides in which the reactivity of the cyano group is so greatly enhanced that it will react with aliphatic or aromatic amines to give virtually quantitative yields of *N*-substituted amidines.[45] The reaction with ammonia is less satisfactory, owing to the formation of the insoluble ammonia–aluminium chloride addition product. Substituted amidines have also been prepared from cyanides and substituted aminomagnesium halides.[46,47] As a preparative method, this is greatly inferior to the aluminium chloride reaction, but it has been applied with some success to the preparation of guanidines and diguanides from cyanamides and cyanoguanidines respectively.[48]

Substituted amidines have also been prepared from ammonia or amines and *N*-substituted imidosulphonates, which were not isolated but prepared *in situ* from a substituted amide and a sulphonyl chloride,[49] or by rearrangement of a ketoxime sulphonate[50] or *N*-substituted acylsulphonimide.[51] This reaction is closely related to von Pechmann's imidochloride synthesis, but is capable of wider application because the aliphatic imidosulphonates are more stable than the corresponding imidochlorides.

When *N*-substituted amidinium salts are treated with ammonia at 100–140° C. an amine is eliminated and the unsubstituted amidinium salt formed. This ammonolysis is remarkably facile, especially in the case of the *N*-arylamidines; and since these compounds are so readily available either from the arylamine sulphonate or by the aluminium chloride method, this reaction forms the basis of what is probably the best general method for the preparation of unsubstituted amidines.[52]

Iminazolines

Most strong bases of the amidine type produce some effect, usually transitory, on the blood pressure, and it has been suggested that this is due to a disturbance of the calcium–potassium balance.[53] Certain *N*-alkylamidines have pronounced anti-cholinergic activity and are also pressor agents, but the degree of activity bears no predictable relation to the chemical constitution.[54] The *N*:*N'*-ethyleneamidines (iminazolines or dihydroglyoxalines) on the other hand have very powerful pressor activity which varies regularly with modifications in the structure.[55] The most active compounds are the 2-arylmethyliminazolines, and at least two members of this group have definite therapeutic value. 2-Benzyliminazoline ('Priscol,' 'Benzazoline') is a potent vasodilator which has been used in the treatment of peripheral vascular disease,[56–58] and 2-(1'-naphthylmethyl)-iminazoline ('Privine,' 'Naphazoline') is a very powerful vasoconstrictor which has found application in rhinology and ophthalmology.[59] These iminazolines probably produce their effects by direct action on the perivascular system; but regardless of the action of the unsubstituted compounds, their *N*-alkyl derivatives all cause a rapid rise in blood pressure and an increase in the heart-rate, apparently by liberation of adrenaline and stimulation of the cardiac muscle.[60]

Derivatives of 2-aminomethyliminazoline were found to possess antihistaminic in addition to pressor activity, and 2-(*N*-benzylanilinomethyl)-iminazoline ('Antistin,' 'Histostab') has been used with considerable success as an antihistaminic agent,[61] since although its histamine number is relatively low it has a high therapeutic index and gives satisfactory clinical results.[62,63] Ethers of 2-hydroxymethyliminazoline also have antihistaminic activity, and the preparation[64–67] and pharmacological evaluation[68,69] of the benzhydryl ether ('Antadryl') have been recorded, but no clinical trials have yet been published.

Iminazolines generally do not appear to possess any marked antibacterial properties, but the quaternary salts derived from higher alkyl and aralkyl substituted iminazolines and iminazoles are efficient antiseptics,[70–72] and 4 : 4′-bis-(2-iminazolinyl)-diphenyl has recently been claimed to combine trypanocidal activity with low toxicity.[73]

2-Substituted iminazolines have been prepared by dehydration of *N*-acylethylenediamines[74] and by heating ethylenediamine with a carboxylic acid or its functional derivatives such as ester, amide, thioamide, iminoether, amidine[75–80] or *N*-substituted amidine.[81] Cyanides also yield iminazolines and higher ring homologues on heating with a free diamine or its basic or neutral salts.[82] The use of the monotoluene-*p*-sulphonate of ethylenediamine is particularly convenient, since this salt is stable, easily prepared from commercial aqueous ethylenediamine, and miscible with organic cyanides when fused. When *N*-alkylethylenediamines are used in this reaction, 2-substituted 1-alkyliminazolines are produced, but *N*:*N*-dialkylethylenediamines yield *N*-dialkylamino-amidines. An ingenious synthesis of 2-substituted 1-aryliminazolines by ring-closure of *N*-aryl-*N*′-2-chloroethylamidines, which are easily prepared from *N*-2-chloroethylimidochlorides, has recently been reported.[83]

References

1 Yorke, W., *Brit. med. Bull.*, 1944, **2**, 60
2 Heathcote, R. St. A., *J. trop. Med. Hyg.*, 1946, **49**, 1, 33
3 Boyd, J. S. K., *Brit. med. J.*, 1950, i, 37
4 Marshall, P. B., *Brit. J. Pharmacol.*, 1948, **3**, 15
5 Gordon, J. J. and Sowden, E., *Biochem. J.*, 1949, **44**, 498
6 Gemmill, C. L., *J. Pharm. exp. Ther.*, 1949, **96**, 173
7 Haedicke, T. A. and Greenspan, E. M., *Amer. J. clin. Path.*, 1949, **19**, 634
8 Harris, J. O., *J. chem. Soc.*, **1947**, 690
9 Ashley, J. N. and Harris, J. O., ibid., **1946**, 567; B.P. 574,484, 574,486 and 574,742
10 Berg, S. S. and Newbery, G., ibid., **1949**, 642; B.P. 598,911
11 Wien, R., Harrison, J. and Freeman, W. A., *Brit. J. Pharmacol.*, 1948, **3**, 211
12 Sen Gupta, P.C., *Lancet*, 1949, ii, 97
13 Wien, R., Harrison, J. and Freeman, W. A., ibid., 1948, i, 711
14 Kohn, F. and Cross, C. D., ibid., 1948, ii, 647
15 Bull, J. P. *et al.*, ibid., 1948, ii, 747
16 Hewitt, L. F., *Brit. J. exp. Path.*, 1948, **29**, 447
16a McClelland and Van Rooyen, C. E., *Canad. J. Res.*, 1949, **27** (*E*), 177
17 Newth, F. H. and Wiggins, L. F., *J. chem. Soc.*, **1947**, 396
18 Ray, F. E., Weisburger, E. K. and Weisburger, J. H., *J. org. Chem.*, 1948, **13**, 655
19 Ashley, J. N., Grove, J. F. and Henshall, T., *J. chem. Soc.*, **1948**, 261
20 Fulton, J. D., *Brit. J. Pharmacol.*, 1948, **3**, 75
21 Levene, H. H. L. and Pyman, F. L., B.P. 544,836; cf. Delaby, R. and Harispe, J. V., *Bull. Soc. chim. Fr.*, 1943, **10**, 580

[22] Andrewes, C. H., King, H., van den Ende, M. and Walker, J., *Lancet*, 1944, i, 777
[23] Evans, D. G., Fuller, A. T. and Walker, J., ibid., 1944, ii, 523; 1945, ii, 336
[24] Fuller, A. T., Tonkin, I. M. and Walker, J., *J. chem. Soc.*, **1945**, 633; B.P. 580, 884
[25] Andrewes, C. H., King, H. and Walker, J., *Proc. roy. Soc.*, 1946 [B], **133**, 20
[26] Forrest, H. S., Fuller, A. T. and Walker, J., *J. chem. Soc.*, **1948**, 1501
[27] Goodwin, L. G. and Marshall, P. B., *J. Pharmacol.*, 1945, **84**, 16
[28] Goldberg, A. A., Kelly, W. and Haynes, F., *J. chem. Soc.*, **1947**, 637
[29] Barber, H. J., *et al.*, ibid., 84
[30] Fuller, A. T., *Biochem. J.*, 1947, **41**, 403
[31] Fields, E. K., *J. Amer. chem. Soc.*, 1949, **71**, 1495
[32] Newbery, G. and Webster, W., *J. chem. Soc.*, **1947**, 739
[33] Partridge, M. W., ibid., **1949**, 2683, 3043
[34] Raison, C. G., ibid., 3319
[35] Cymerman, J. and Short, W. F., ibid., 703; B.P. 614,072
[36] Cornforth, J. W. and Huang, H. T., ibid., **1948**, 1960
[37] Ellinger, L. P. and Goldberg, A. A., ibid., **1949**, 263
[38] Barber, H. J., Wilkinson, J. H. and Edwards, W., *J. Soc. chem. Ind.*, 1947, **66**, 411; B.P. 581,695
[39] Barber, H. J., B.P. 559,015
[40] Shriner, R. L. and Neumann, F. W., *Chem. Rev.*, 1944, **35**, 351
[41] Oxley, P. and Short, W. F., *J. chem. Soc.*, **1946**, 147; B.P. 573,266
[42] Oxley, P., Partridge, M. W., Robson, T. D. and Short, W. F., ibid., 763; B.P. 583,586
[43] Partridge, M. W. and Short, W. F., ibid., **1947**, 390; B.P. 595,965
[44] Oxley, P., Partridge, M. W. and Short, W. F., ibid., **1948**, 303; B.P. 604,032
[45] Idem, ibid., **1947**, 1110; B.P. 598, 453
[46] Hullin, R. P., Miller, J. and Short, W. F., ibid., 394
[47] Wellcome Foundation, Ltd., B.P. 619,659
[48] Birtwell, S., Curd, F. H. S. and Rose, F. L., *J. chem. Soc.*, **1949**, 2556
[49] Oxley, P., Peak, D. A. and Short, W. F., ibid., **1948**, 1618
[50] Oxley, P. and Short, W. F., ibid., 1514; B.P. 577,478; 579,303
[51] Idem, ibid., **1947**, 382; B.P. 590,131
[52] Idem, ibid., **1949**, 449; B.P. 612,980
[53] Fastier, F. N., *Brit. J. Pharmacol.*, 1949, **4**, 315
[54] Djerassi, C. and Scholz, C. R., *J. Amer. chem. Soc.*, 1947, **69**, 1688; U.S.P. 2,425,730
[55] Scholz, C. R., *Ind. Eng. Chem.*, 1945, **37**, 120
[56] Grimson, K. S., Reardon, M. J., Marzoni, R. A. and Hendrix, J. P., *Ann. Surg.*, 1948, **127**, 968
[57] Winsor, T. and Ottoman, R., *Proc. Soc. exp. Biol. Med.*, 1949, **70**, 647
[58] Rogers, M. P., *J. Amer. med. Ass.*, 1949, **140**, 272
[59] Meier, R., Gross, F. and Eichenberger, E., *Helv. Physiol. Pharmacol. Acta*, 1949, **7**, 230
[60] Gowdey, C. W., *Brit. J. Pharmacol.*, 1948, **3**, 254; 1949, **4**, 45
[61] Ciba, Swiss Pat. 245,888–245,900; U.S.P. 2,449,241
[62] Huttrer, C. P., *Experienta*, 1949, **5**, 53
[63] Landau, S. W. *et al.*, *Bull. Johns Hopkins Hosp.*, 1948, **83**, 330, 343, 356
[64] Djerassi, C. and Scholz, C. R., *J. org. Chem.*, 1948, **13**, 830
[65] Dahlbom, R. and Sjögren, B., *Acta chem. scand.*, 1948, **1**, 777
[66] Protiva, M. and Urban, J., *Coll. Czech Chem. Communications*, 1948, **13**, 326
[67] Dahlbom, R., *Acta chem. scand.*, 1949, **3**, 32, 93
[68] Cattaneo, R. and Rosso, S., *Minerva Med.*, 1949, **40**, I, 623
[69] Testoni, F., ibid., 690
[70] Monsanto Chem. Co., U.S.P. 2,392,326, 2,404,300
[71] Shepard, E. R. and Shonle, H. A., *J. Amer. chem. Soc.*, 1947, **69**, 2269
[72] Kyrides, L. P. *et al.*, *J. org. Chem.*, 1947, **12**, 577
[73] Ciba, B.P. 618,039
[74] Aspinall, R., *J. Amer. chem. Soc.*, 1939, **61**, 3195
[75] Klarer, W. and Urech, E., *Helv. chim. Acta*, 1944, **27**, 1762
[76] Ciba, B.P. 608,295; 608,296
[77] Løvens, B.P. 608,067
[78] Aktiebolaget Recip., B.P. 620,339
[79] Kyrides, L. P., U.S.P. 2,457,047

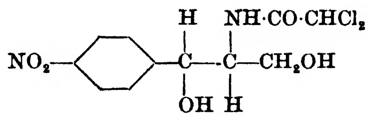
[80] Melander, B. O. and Askelöf, E. E. A., Swed. Pat. 121,537
[81] Short, W. F. and Oxley, P., B.P. 614,032
[82] Oxley, P. and Short, W. F., *J. chem. Soc.*, **1947**, 497 ; B.P. 591,683
[83] Partridge, M. W. and Turner, H. A., ibid., **1949**, 1308

CHLORAMPHENICOL (CHLOROMYCETIN) (H. J. Barber, Ph.D., F.R.I.C.)

May and Baker Ltd.

THIS remarkable substance was born an antibiotic but has developed as a synthetic medicinal chemical. It therefore finds a place both in the Antibiotic Section of these Reports and in this section. It is probably unique among naturally occurring substances in containing both a chlorine and a nitro group, though recently another 'natural nitro group' has been found as β-nitropropionic acid, a constituent of the glycoside hiptogen from the bark of the tree *Hiptage mandoblata*.[1] The importance of chloramphenicol justifies a detailed report on the chemistry.

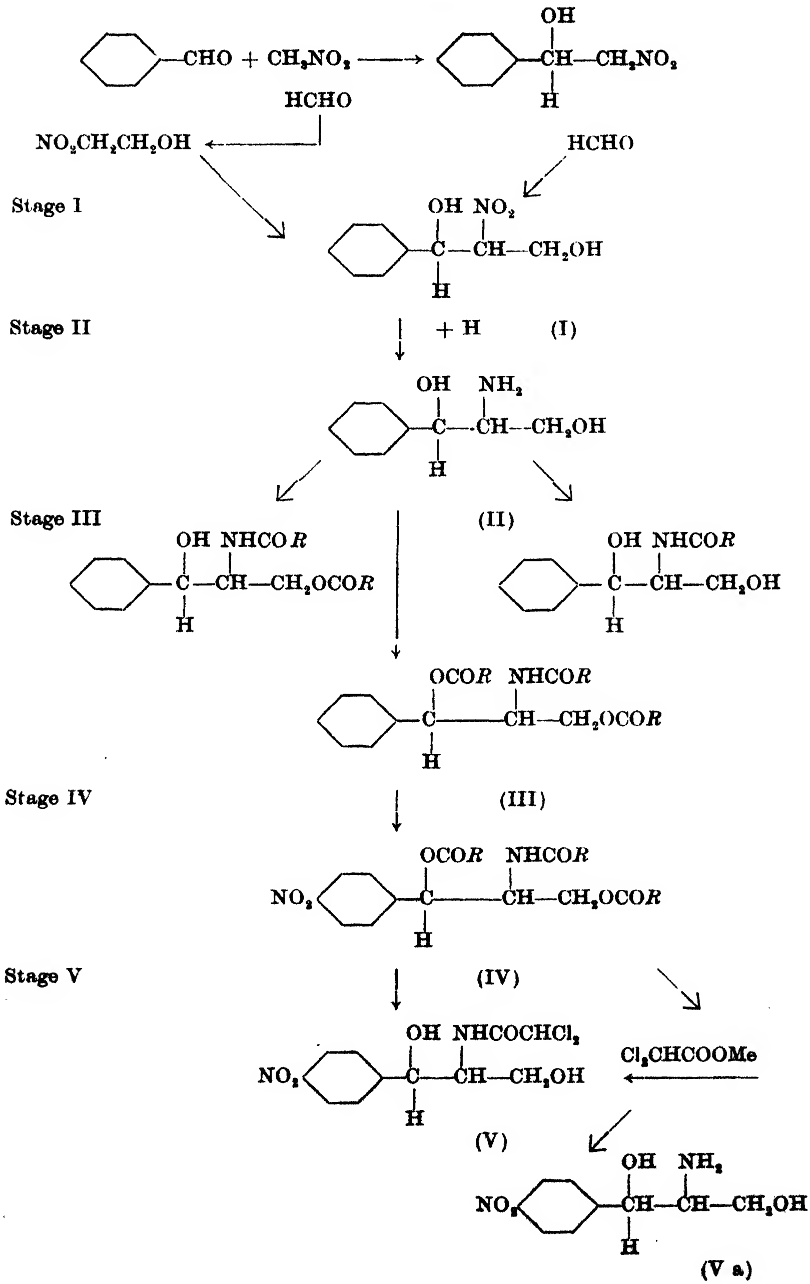
The degradative and ultra-violet absorption spectra studies which led to the structure now assigned to chloramphenicol are reported by a Parke, Davis group.[2] It is D-(−)-threo-2-dichloracetamido-1-*p*-nitrophenyl-1 : 3-propane-diol:



The stereochemical considerations are most conveniently classified by reference to the ephedrine series, the active antibiotic being regarded as a derivative of a substituted L-nor-ψ-ephedrine.

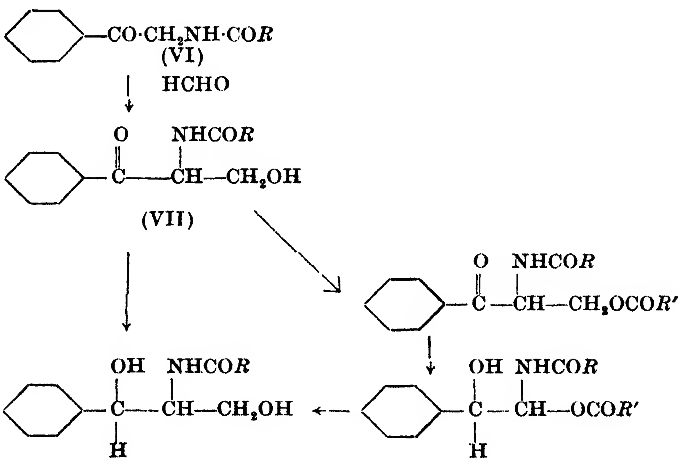
The two main groups of synthetic routes are dealt with in further papers from the Parke, Davis group[3] and in two patent applications[4] recently laid open for public inspection. The syntheses may be conveniently designated 'nitropropanol' or 'aminoacetophenone' routes respectively. Each involves at one stage the key intermediate 1-phenyl-2-aminopropane-1 : 3-diol. It should be noted at this point that the applications are not confined to chloramphenicol itself, but to the extensive classes of substituted and homologous chloramphenicols. But for simplicity the synthesis will be considered for chloramphenicol itself in the first place. To denote the diastereoisomers, the terms 'regular' and 'pseudo' (ψ) are used in the patents and 'erythro' and 'threo' in the papers ; the former are used here.

The nitropropanol routes are summarized in the following flow diagram :



The synthesis comprises five main stages. The phenylnitropropanediol (I) can be prepared by either of the variants shown, which in essence differ only in the order in which the three reactants benzaldehyde, formaldehyde and nitromethane are combined. The condensation of β-nitroethanol with benzaldehyde appears to be the preferred alternative and the product is isolated as sodium salt. The reduction is carried out catalytically (palladium oxide) under mild conditions in glacial acetic acid. The more soluble ψ-isomer is separated in a chloroform crystallization. The acylation prior to nitration presents many possible variations. *N*-Dichloracetylation can be achieved with methyl dichloracetate and then di-*O*-acetylation with acetic anhydride in pyridine, the *O*-acyl group being removed preferentially after nitration. Alternatively triacetylation can be carried out then nitration, then complete hydrolysis and subsequent *N*-dichloracetylation. If optical resolution of the ψ-isomer is required the DL-ψ-1-*p*-nitrophenyl-2-aminopropane-1 : 3-diol (V a) is converted to the tartrates with D-tartaric acid and crystallized from methanol; the D-tartrate of the L-ψ-base separates first.

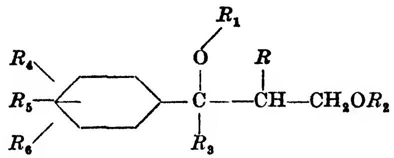
The 'aminoacetophenone' route possesses certain features in common with the 'nitropropane' route as will be apparent from the following flow diagram (for chloramphenicol itself):



The first stage of methylolation of benzamidoacetophenone (VI) is carried out under mild alkaline conditions and it appears to be necessary to stop the reaction after a few minutes only. The crude product (VII) is reduced catalytically (Raney nickel or palladium oxide) to the crude benzamidopropane-1 : 3-diol (VIII). This is purified by crystallization from methanol and ethanol, the ψ-form being the less soluble. This patent does not describe specifically the conversion of substance (VIII) to chloramphenicol but the route is obvious.

Each application claims in effect a general method of preparing not

only chloramphenicol itself but numerous classes of substances which may be derived from the general formula



where R is $-NO_2$, $-NH_2$ or an acylamino radical such as a lower aliphatic acylamino, a halogen-substituted lower aliphatic acylamino, a benzoylamino, a substituted benzoylamino and the like radicals; R_1 and R_2 are the same or different and represent hydrogen or acyl radicals of the kind already defined; R_3 is hydrogen or lower alkyl; R_4 and R_5 are the same or different and represent hydrogen, halogen, lower alkyl or lower alkoxyl radicals; and R_6 is hydrogen or an $-NO_2$ group. It will be clear that the 52 claims and 21 claims in the respective patents aim at protecting a very considerable field.

It is to be expected that other, probably improved, syntheses will be disclosed in the near future.

References

1 Carter and McChesney, *Nature*, 1949, **164**, 575
2 *J. Amer. chem. Soc.*, 1949, **71**, 2458
3 Ibid., 2463, 2469
4 Pat. Appl. Nos. 32,505/48 (aminoacetophenone), 32,506/48 (nitropropanol)

SYNTHETIC CURARIZING AGENTS (H. J. Barber, Ph.D., F.R.I.C.)

May and Baker, Ltd.

THE term 'curarizing agent' is mainly one of convenience and links the synthetic substances with curare in a historical, as distinct from a precise, pharmacological sense. The main action of curare is paralysis of muscle to excitation through its nerve, but it also produces secondary effects, as indeed do all the synthetic compounds, though these secondary effects may differ both in degree and kind. Some of the side reactions can be overcome by the use of other drugs which will counter them without impairing the main function of the 'curarizing' agent. But these adjuvants may in their turn introduce new effects of an undesirable kind and it will be obvious, therefore, that the chief objective in the search for new synthetic curarizing drugs is freedom from side reactions with adequate but not necessarily maximum activity. Excellent reviews and discussion of the pharmacology of this group, particularly in relation to chemical constitution, have been given by Paton[1] and by Bovet[2] and it is only necessary to refer briefly to the main developments.

The application of the properties of certain of the curare alkaloids to obtain adequate muscular relaxation in abdominal surgery without inducing a dangerous depth of anaesthesia came into clinical practice about 1944 following pioneer work by Griffiths and Johnson in the U.S.A.[3] King's earlier chemical studies[4] on the curare alkaloids undoubtedly contributed materially to this development. Initially partially purified alkaloidal preparations were used (e.g. 'Intocostrin' was described in the New and Non-Official Remedies of the U.S. Council on Pharmacy and Chemistry 1945 as 'containing therapeutically desirable constituents of curare' and was marketed by E. R. Squibb and Sons) but pure D-tubocurarine chloride ['Tubarine' (Burroughs, Wellcome)] soon became available and achieved a definite place as an adjuvant to anaesthesia in surgery. But it suffers from the inherent disadvantage of being derived from a natural raw material of comparatively limited availability (*Chondrodendron tomentosum* from the Amazon region).

'Myanesin' (α-β-dihydroxy-γ-(2)methylphenoxypropane) introduced early in 1947 appears to have been the first synthetic 'curarizing' substance to be used in this country in place of curare,[5] although Berger and Bradley in discussing its effect on muscle make it clear that its mode of action is quite different from that of curare and the substance is therefore not a curare substitute. Its pharmacological actions are probably due to its depressant action on the spinal cord whereas curare suppresses the action of acetylcholine in transmitting impulses at the myoneural junction. Meanwhile, French workers, notably Bovet and his collaborators, were studying a number of synthetic quaternary ammonium compounds including bis-(8'-quinoloxy)-1 : 5-pentane diethiodide, which had a certain structural resemblance to a fragment of the tubocurarine molecule and which was the first compound to have marked activity.[7] This was the subject of a Rhône-Poulenc patent.[8] Further investigation showed that other and simpler molecules containing the quaternary ammonium group had intense curare-like action,[9,10] and this eventually led to the substance tri-(β-diethylaminoethoxy)-1 : 2 : 3-benzene triethiodide (F.2559, R.P.3697, 'Flaxedil'),[11,12] also the subject of a patent application.[13] The use of this substance in 200 cases was favourably reported in France by Huguenard and Boué.[14] British publications[15,16] have described the pharmacology of this substance and its use in abdominal surgery.[17] It appears to act in a very similar manner to tubocurarine but is less liable to facilitate the release of histamine and thus produce a fall in blood-pressure. About 120 mg. is needed to produce the same effect as 15 mg. tubocurarine and the effect is similarly reversed by eserine or neostigmine.

Independently of this work, Ing and Barlow had pursued the same idea that the action of tubocurarine stemmed from the presence of two cationic groups an optimal distance apart and accordingly examined a number of substances in which the two quaternary ammonium groups [$-\overset{+}{N}(CH_3)_3$, $-\overset{+}{N}(C_2H_5)_3$, strychninium$^+$, quinolinium$^+$] were separated by polymethylene chains $(CH_2)_n$ where $n = 2 - 13$ (omitting $n = 6$). Of these they found maximum activity at C_{10}.[18] Paton and Zaimis[19] drew attention to the very varied responses produced in different test organs and animals by the individual compounds in this group and stressed the need

for wide pharmacological testing when searching for activity which might lead to clinical application in this field. Since 'C_8' and 'C_{10}' (these compounds were conveniently designated by the number of carbon atoms in the chain) were highly active but were not antagonized, as was tubocurarine, by eserine or neostigmine, it was essential to find a suitable antidote before clinical use could be contemplated. Later Paton and Zaimis,[20] as a result of further study of C_{10} during which they found that C_5 was an antagonist, suggested that it might be a substitute for tubocurarine chloride and some preliminary experiments on man, described by Organe, Paton and Zaimis,[21] led to clinical trials (sponsored by the Medical Research Council).

Clinical experience has been described by Organe,[22] by Hewer, Lucas, Prescott and Rowbotham[23] and further reports of its use continue to appear. It is to be regarded as a true curarizing agent in the sense that it blocks neuromuscular action but presumably by a different mechanism since the action is not antagonized by eserine, whereas that of tubocurarine and Flaxedil is. It has been given the approved name of decamethonium iodide and has been marketed under various trade names [e.g. 'Eulissin' (Allen and Hanbury), 'Syncurine' (Burroughs, Wellcome)]. It is too early to give a firm assessment of the place of this substance. As with all new drugs, certain disadvantages have become apparent with more experience and while it produces good muscular relaxation, this is not achieved without respiratory paralysis. Moreover, C_5 or pentamethonium iodide has a strong autonomic blocking effect which leads to severe fall in blood-pressure and its use as an antidote to C_{10} is difficult to justify. There are many other occasions apart from surgery under anaesthesia where muscular relaxation is indicated, notably in electroconvulsion therapy, and favourable experience in this use with C_{10} has been reported by Hobson and Prescott,[24] and also with 'Flaxedil.' In many other conditions associated with muscle spasm in various forms 'Myanesin,' given orally, show promise of being more useful than as an adjuvant in surgery where its haemolytic action is prejudicial. The current status of muscle relaxants in anaesthesia is reviewed by Woolmer[25] and it is clear that the developments discussed do in fact already represent significant progress. Further synthetic work coupled with wider and more detailed pharmacological studies in this field may be expected to reveal new applications to human therapy.

References

1 *J. Pharm. Pharmacol.*, 1949, **1**, 273
2 *Experientia*, 1948, **4**, 325
3 *Anaesthesiology*, 1942, **3**, 418
4 *J. chem. Soc.*, **1935**, 1381
5 Mallinson, F. B., *Lancet*, 1947, i, 98
6 Ibid., 97
7 *C.R. Acad. Sci., Paris*, 1946, **223**, 597
8 B.P. 626,007
9 *C.R. Acad. Sci. Paris*, 1947, **224**, 1733
10 Ibid., **225**, 74
11 Ibid, 956
12 *Arch. int. Pharmacodyn*, 1949, **80**, 172
13 B.P. Appl. No. 15,479/48

[14] Soc. franç. d'Anesthesie et d'Analgesie, June 19, 1947
[15] Mushin, Wien, Mason and Langston, *Lancet*, 1949, i, 726
[16] Bubring and Depierre, *Brit. J. Pharmacol.*, 1949, **4**, 22
[17] Wilson and Gordon, *Lancet*, 1949, **2**, 504
[18] *Nature*, 1948, **161**, 718; *Brit. J. Pharmacol.*, 1948, **3**, 298
[19] *Nature*, 1948, **161**, 718
[20] Ibid., **162**, 810
[21] *Lancet*, 1949, i, 21
[22] Ibid., 773
[23] Ibid., 817
[24] Ibid., 819
[25] *The Practitioner*, 1949, **163**, 320

MISCELLANEOUS REACTIONS, METHODS, Etc. (H. J. Barber, Ph.D., F.R.I.C.)

May and Baker, Ltd.

THE rapidly increasing literature on the use of lithium aluminium hydride, $LiAlH_4$, as a reducing agent emphasizes its importance and several technological applications are described elsewhere in this Report. Bachmann[1] describes the semi reduction of a dicarboxylic ester to an ester–alcohol, one ester group remaining unattacked, presumably for steric reasons. This provided a new route to *cis*-9-methyl-1-decalone. Nitriles can be converted to aldehydes by controlled reaction with $LiAlH_4$ according to a claim by Lester Friedman.[2]

The interest in long-chain fatty alcohols has stimulated much interest in the reduction of fatty glycerides and esters and the classical Bouveault–Blanc sodium/alcohol reduction has been studied in much detail recently. The Procter and Gamble plant for reducing coconut oil by a process based on work by Dupont is described.[3] The essential features involve the addition of the glyceride (dried and with low fatty acid content) mixed with toluene and the theoretical weight of a suitable secondary alcohol (methyl amyl alcohol) to stirred molten sodium in boiling toluene at a rate such that no unreduced glyceride accumulates. Similar techniques should be applicable to pure carboxylic esters and, with adequate safeguards, this essentially cheap reduction should find wider application. It may be noted that double bonds are usually left intact.

Acyl migration between O and N in β-amino-alcohols, probably through intermediate cyclic systems which can be oxazolines, is well known and is important in the interconversion of ψ- and regular stereoisomers such as L-ephedrine and D-ψ-ephedrine. Further work in this field by Welsh,[4], by Fry[5] and by Fodor *et al.*,[6] may be noted. The latter claim that the more facile acyl migration N $\rightarrow$ O in the ψ series can be used for separation from the regular. Oxazoline formation in relation to threonine is discussed under the heading of amino-acids.

The well-known alkylation of amines by means of aldehydes or ketones and formates or formic acid has many applications. The survey by

Staple and Wagner[7] is therefore valuable. They classify the different versions of the reaction known variously as the Leuckart or Wallach reaction and discuss the favourable reaction conditions from a consideration of possible mechanisms. They conclude that in general it is preferable to obtain a complete condensation between amine and carbonyl compound for best yield. Initial formylation was unfavourable and this is in accord with the moderate yields recorded by Bunnett and Marks[8] in their preparation of tertiary amines by the Leuckart reaction. The application to a heterocyclic amine is the subject of a patent by Pyridium Corporation[9] who claim alkylation of 2-aminopyrimidine, presumably to provide intermediates for pyrimidine antihistaminics.

A method of preparing substituted α-aminoacetophenones and thence by reduction the α-phenyl-β-aminoethanols is claimed in a patent by Philips Gloeilampenfabricken.[10] Substituted aminoacetonitriles are condensed with phenols, phenol ethers or esters in presence of $AlCl_3$, the usual intermediate imine being hydrolysed to the ketone.

$$R\mathrm{OC_6H_5} + \mathrm{CN{\cdot}CH_2N}\langle^{R_1}_{R_2} \longrightarrow R\mathrm{{\cdot}O{\cdot}C_6H_4CO{\cdot}CH_2N}\langle^{R_1}_{R_2}$$

The following have been noted as having potential interest in this field :

Ritter and Kalish[11] report a new reaction of nitriles with certain alkenes in presence of concentrated sulphuric acid which leads to acylamido compounds. Thus with *iso*butene and acetonitrile

$$\mathrm{Me_2C = CH_2 + MeCN} \xrightarrow{\mathrm{H_2SO_4}} \mathrm{Me_3C{\cdot}NHCOMe}$$

allyl benzene and acetonitrile give an amide hydrolysable to amphetamine, but the over-all yield is only moderate.

Hass and Bender[12] use sodium 2-propane nitronate as a means of converting substituted benzyl halides to benzaldehydes, claiming yields of 68–77%. The nitronate is converted to acetone oxime.

$$R_6\mathrm{{\cdot}CH_2Br + Me_2C{:}NO_2Na} \longrightarrow R\mathrm{{\cdot}CHO + Me_2C : NOH + NaBr}$$

Hopf and Ohlinger[13] give preparative details for the synthesis of a number of aromatic amides from the hydrocarbon and carbonyl chloride. A normal Friedel–Crafts technique is used and yields of 85–95% are claimed. The carbamyl chloride is made from phosgene and ammonia at 400° c. and is stabilized by conversion to a molecular compound with $AlCl_3$ or $FeCl_3$.

Use of trifluoracetic anhydride as a novel esterifying agent for carboxylic acids and alcohols or phenols is described in a preliminary note from M. Stacey *et al.*[14]

Some workers still seek alternative routes even to cheap and well-established pharmaceutical intermediates. Thus for aryl malonates Cope and Field[15] record a number of failures and one limited success of some general interest, though hardly the basis for an economic technical

process. The aryl Grignard is condensed at low temperature with diethyl mesoxalate and the aryl tartronate is then converted to the aryl chloromalonate which is catalytically reduced to the aryl malonate.

The possible role of the bromine cation Br^+ in bromination reactions has been suggested by Derbyshire and Waters[16] as a result of an observation that bromide-free hypobromite is a much more active brominating agent for aromatic hydrocarbons than free bromine. The development of this conception might well lead to some interesting practical applications.

References

1 *J. Amer. chem. Soc.*, 1949, **71**, 3222
2 *Chem. Engng. News*, 1949, **27**, 2923
3 *Ind. Eng. Chem.*, 1949, **41**, 438
4 *J. Amer. chem. Soc.*, 1949, **71**, 3500
5 *J. org. Chem.*, 1949, **14**, 887
6 Ibid., 335
7 Ibid., 559
8 *J. Amer. chem. Soc.*, 1949, **71**, 1587
9 B.P. 615,931
10 B.P. Appl. No. 10,382/48
11 *J. Amer. chem. Soc.*, 1949, **71**, 4045
12 Ibid., 1767
13 *Angew. Chem.*, 1949, **61**, 183
14 *Nature*, 1949, **164**, 705
15 *J. org. Chem.*, 1949, **14**, 586
16 *Nature*, 1949, **164**, 446

PHOTOGRAPHIC MATERIALS AND PROCESSES

By H. BAINES, D.Sc., F.R.I.C., Hon. F.R.P.S., P. C. BURTON, B.Sc., and A. K. SOPER, M.Sc., A.R.I.C.

THE production of sensitive materials in this country during the past year has, owing to the continuing sellers' market at home and the needs of the export drive, been limited only by the capacity of the industry. Under these conditions, it is not surprising that manufacturers have concentrated on the production of well-established lines, and that except in the special fields of colour photography, photomechanics, and nuclear-particle emulsions, the year has not been remarkable for improvements in the quality or range of materials marketed. The needs of the amateur have been met to some extent by an increase in the supply of roll-films, but materials for colour photography are still in very short supply throughout Europe. Perhaps the most striking advance we have to report is one that will be regarded with mixed feelings by chemists, namely the invention of 'xerography,' a new non-silver photographic process that depends only on the simple physical phenomena of photo-conductivity and electrostatic attraction.

Theory of sensitivity and latent-image formation

It is well known that the photographic latent image—which in a highly-sensitive material represents only about one 'changed' molecule in a thousand million—can be studied only by indirect methods. One method is to study the photolytic action of large amounts of light and extrapolate back to the latent-image region. Another is to attempt to deduce the mechanism of latent-image formation theoretically from the concepts of crystal physics. Another is to study the developed images resulting from various combinations of exposures and chemical treatments and interpret the results in terms of the processes occurring before development. Each of these approaches is exemplified in the papers to be reviewed.

Mitchell[1] has published a further elaboration of the theoretical ideas reviewed in last year's Report. He explains the experimental results of Stasiw and Teltow[1a] on the optical properties of large silver halide crystals containing traces of silver sulphide on the supposition that the dissolved silver sulphide takes the form of S^- ions accompanied by F–centres (electrons trapped at vacant halide-ion sites). This leads to a consideration of latent-image formation in photographic emulsions. The 'sensitivity speck' that acts as a nucleus for latent-image formation is considered to be a small neutral aggregate of F–centres. Mitchell discusses the properties that such an aggregate would have, and argues that it would grow only very inefficiently under illumination, but on reaching a certain size would acquire a positive charge and thereafter grow efficiently.

The latent-image speck is supposed to be such a positively-charged aggregate. No comment on this theory has yet appeared.

Meidinger,[2] continuing his researches on the production of photolytic silver (determined chemically) in silver halide–gelatin emulsions, has carried out a comprehensive investigation into the quantum efficiency (ϕ) of the process. The exposures used produced some 10^{14}–10^{15} atoms of photolytic silver per cm^2. of the emulsion layer, whereas latent-image exposures would be expected to produce only 10^8–10^{12}, or in the case of a Lippmann (very fine-grain) emulsion, 10^{13}–10^{14} atoms.

He finds that for ordinary bromide or iodobromide emulsions ϕ is about 0·1 at room temperature, or 0·6 if the emulsion is impregnated with a bromine acceptor, e.g. sodium nitrite. A Lippmann emulsion gave a value of only 10^{-4}, rising to 0·13 in the presence of an acceptor. In this case, merely moistening with water was sufficient to bring about the rise from 10^{-4} to 0·13. In the presence of an acceptor, ϕ rose nearly to unity at 100° c.; this result is perhaps a little doubtful, since no account was taken of the increase of absorption coefficient with temperature. On lowering the temperature, ϕ fell rapidly, becoming vanishingly small a little below − 100° c. The effect of the acceptor disappeared below −100° c. for AgBr emulsions, and below 20° c. for AgCl. Acceptors had no effect on the ordinary photographic sensitivity as measured after development, except in the case of the Lippmann emulsion, where a roughly fourfold increase was observed. This was interpreted to mean that the quantum efficiency for latent-image formation in the absence of an acceptor, which of course could not be observed directly, must have been at least as great as the observed efficiency for photolysis in the presence of an acceptor (0·6) or at least one-quarter as great (i.e. 0·03) in the Lippmann case. A further proof of the point was that the number of latent-image silver atoms produced in the Lippmann emulsion, calculated on the basis of the low value of ϕ (10^{-4}), came out to be less than the observed number of developed grains.

In another paper,[3] Meidinger uses a similar argument to prove that the amount of latent-image silver produced at the surface of the grain (where it is accessible to the developer) cannot be accounted for merely by the quanta absorbed in the monomolecular surface layer of the grain. He analyses the sensitivity of the material into a number of factors—absorption, quantum efficiency of photolysis, etc.—and shows that the number of silver atoms calculated from the surface absorption alone is less than the observed number of developed grains. This agrees with the accepted view that latent-image formation is a coagulation process, in which the site at which the quantum is absorbed, whether inside the grain or on its surface, has no influence on the result.

The bewildering variety of apparently unrelated photographic 'effects' has been notably reduced in recent years by the realization that latent-image specks are of various kinds. In its initial stages of growth the speck is too small to be developed under ordinary conditions, but can be detected by applying a second, auxiliary exposure, which builds it up to the developable size. Specks formed inside the grains can be detected by using a developer solution containing a silver halide solvent after destroying any superficial nuclei by oxidation. Berg[4] has given a useful review of the

properties of the 'sub-image' revealed by post-exposures, which leads to a consideration of the distribution of sizes of the specks formed by a given exposure in relation to its magnitude and intensity, and an explanation of the way in which the rate of development depends on the intensity of exposure. Further confirmation of the 'sub-image theory' comes from Vanselow, Quirk, and Leermakers[5] in a study of latent-image intensification (i.e. a process that renders the sub-image developable) by sodium perborate solutions. As in the case of post-exposures, the intensification becomes small (though still appreciable) with long development-times, vanishes when the latent image is sufficiently aged, and occurs after high-intensity but not low-intensity exposures. Berg and Ford[6] have studied the distribution of the latent image between the surfaces and interiors of the grains, using a non-solvent physical developer (*a*) before fixation and (*b*) after oxidation of the surface image and fixation; the results agree well with those obtained in earlier work with chemical development, and again give no reason for suspecting that there is any intrinsic difference between the internal and superficial kinds of speck.

Arens[7] has published a study of reversal phenomena obtained with emulsions that form predominantly internal latent image. The emulsions and the mechanism of the reversal appear to be essentially similar to those described by Knott and Stevens and reviewed in a previous report.[8] Arens considers that the same mechanism explains the Sabattier reversal observed with emulsions that give a normal latent-image distribution, the supposition being that in an ordinary exposed emulsion a small proportion of the grains have internal but not superficial latent-image specks. He was not able, however, to demonstrate the presence of such grains directly.

In an investigation of the Herschel effect, or bleaching of the latent image by exposure to red or infra-red light, Kornfeld[9] has found evidence confirming the view that the effect is essentially a redistribution rather than a destruction of the latent-image substance. She points out that the effect provides a sensitive means of gauging the stability or size of the latent-image specks, and confirms the older findings that images produced by low-intensity exposure are more stable than those produced at high intensities, and that the specks spontaneously become more stable on ageing. Sauvenier and Winand[10] have found that the Herschel effect can be obtained when the initial image is produced by α-rays instead of light.

Some years ago Debot discovered that plates that have been heavily exposed and then treated with an oxidizer to remove the surface image become sensitive to the red and infra-red. The spectrogram shows a maximum at 880mμ. and ends abruptly at 1150mμ. This sensitivity was thought to result from a transfer of the internal silver to the surface. Hautot and Sauvenier[11] have now supplemented the earlier work by showing that the amount of internal image is reduced by the red-light exposure. Another finding, which is not so easy to understand, is that the transfer is greatly facilitated by the presence of a bromine acceptor.

A related but distinct effect is the sensitization of the photolytic decomposition of silver halide into silver and halogen produced by photolytic silver. Meidinger[12] has carried out a comprehensive investigation of the effect, which confirms and extends our previous knowledge (*see*

last year's Report). In the presence of a halogen acceptor, he finds a quantum efficiency of 0·1 at 546mμ. for the silver-sensitized photolysis in AgBr emulsions, falling sharply to 0·007 at 700mμ.; in AgCl the efficiency is 0·1 at 436mμ. and 0·004 at 578mμ. The spectrum is thus quite unlike the spectrum of the Herschel and Debot effects. The acceptor gave a tenfold increase of efficiency in AgBr but had no effect on AgCl. It is possible that the Debot effect represents merely a redistribution of the silver, the primary action being the ejection of an electron from the silver speck, whereas in the sensitization of photolysis the silver particles act in the same way as sensitizing-dye molecules, by transferring the absorbed energy to the crystal. On this simple view, however, the effect of halogen acceptors on the Debot effect and the change of efficiency with wavelength in the other effect are not easy to understand.

In 1947 Vassy *et al.* reported that on the storage of a Lippmann plate[8,13] or a cinematograph positive film[14] a peak of sensitivity developed in the near ultra-violet. Farnell and Pinoir[15] now report that they have been unable to reproduce the phenomenon, which remains on record as one of those isolated and unexplained curiosities in which the photographic literature is so rich.

Recording of nuclear-particle tracks

The direct recording of the tracks of nuclear particles in the photographic emulsion is now a standard technique in nuclear physics. Interest in this field has centred around the question of recording the tracks of electrons and fast particles of minimum ionizing power. In a paper read early in 1948 but published only recently, Berriman[16] stated that the most sensitive emulsion then available would record electrons of energy 50–80 ke.v., and on this basis estimated that the number of ionizations needed for the developability of a grain was about the same whether the ionizing agent was a nuclear particle or light ($\sim$ 50), and that roughly a threefold increase of sensitivity was needed if particles of minimum ionizing power—and thus any particles whatsoever—were to be recorded. Webb,[17] in an excellent review and theoretical discussion of the whole field, came to somewhat similar conclusions. In December, 1948, Berriman[18] reported that a higher sensitivity had been achieved, and presented evidence that strongly suggested that particles of minimum ionizing power could now be recorded. Herz[19] has shown that although electron tracks cannot be recognized individually in an ordinary X-ray emulsion exposed to X-rays, their presence can be detected by the increase of granularity that occurs with increasing quantum energy of the X-rays. The fading of nuclear-particle tracks continues to attract attention; Albouy and Faraggi[20] report that humidity, atmospheric oxygen, and a high p_{H} favour fading; in an atmosphere of dry nitrogen no fading of α-particle tracks was observed in the emulsions studied.

Emulsions

Basic materials and manufacturing processes.—The dislocation of supplies during the way compelled Swiss manufacturers to make use of new and untried grades of gelatin. To meet this situation a method of

testing and classifying gelatins was evolved by Ammann-Brass, who has now published a series of papers on the subject.[21] The method consists in ripening a series of simple silver chloride emulsions for different times with different concentrations of the given gelatin and measuring the turbidity of each sample. The family of curves relating turbidity to concentration and ripening time is characteristic of the gelatin. Thus inert gelatins can be distinguished from those that retard grain-growth and those that give strong sulphur-sensitization—the last giving a minimum in the turbidity–concentration curve. The last paper shows the effect of removing the active constituents of an active gelatin and the effect of adding a sensitizer to an inert gelatin. Steigmann[22] has suggested independently that Ammann's basic procedure should be supplemented by testing the gelatin not only in its natural state but also after removal of sensitizers and retarders.

Damschroder and Kauffman[23] have patented a method of deactivating gelatin or other proteins by treatment with a finely divided metal whose sulphide is insoluble, e.g. platinum or nickel. Pouradier and Abribat[24] have given a stimulating discussion of the structure, constitution, and molecular-weight distribution of gelatin and the effect of p_H.

Patents on the use of binding media other than gelatin continue to appear. Lowe[25] describes the preparation of polyvinyl alcohol coatings, which are gelled by including a small amount of $Zr(NO_3)_4$ or a similar metallic compound and then fumed with ammonia; in another patent[26] the zirconium is added in alkaline solution in the form of a polyalcohol complex (in order to prevent the precipitation of ZrO_2 at the high p_H). Staehle[27] describes a cold-setting preparation of polyvinyl alcohol including a boron compound, e.g. H_3BO_3, which is fumed with a volatile base after coating. Barnes and Ney[28] claim that gelatin coatings can be improved by including a few per cent. of an interpolymer of acrylic acid derivatives and their amides.

Sauvenier has published further results of his studies on the preparation of conventional silver bromide emulsions, dealing with the effect of precipitation, ripening, and after-ripening on spectral sensitivity[29] and the influence of excess potassium bromide on X-ray and light sensitivity.[30]

New optically sensitizing dyes.—We distinguish *optical* or spectral sensitizers from *chemical,* i.e. spectrally non-selective, sensitizers. It is difficult to write an account of this field that goes beyond a mere list of references and chemical formulae. The literature consists mainly of patents, of which a large number are published every year; although some of the claims are of greater chemical interest than others, it is generally not possible to assess their relative importance from the photographic point of view.

Progress continues to be reported in the interesting field of polymethine dyes containing three or more heterocyclic nuclei. Hamer, Rathbone and Winton[31] have extended their syntheses of neocyanines reported last year to dyes containing two similar and one dissimilar nuclei separated by a trimethine and a pentamethine chain, and have prepared for the first time neocyanines containing three dissimilar nuclei. These dyes, it is stated, generally have only weak sensitizing properties. A patent from Anish[32] describes the preparation of trinuclear iminol cyanines, and one

from Wilson[33] deals with trinuclear dyes containing more than one complete styryl nucleus.

Additional examples of cyanine dyes containing alkylene bridges in various positions in the molecule are described by Brooker[34] (*N*:*N'*-alkylene type), by Schwarz and de Smet[35] (dyes containing a bridge between the nuclear nitrogen and the α-methine carbon atom), and in a Gevaert patent[36] (tetranuclear dyes formed by linking the polymethine chains of two binuclear dye molecules with an alkylene or oxy-alkylene bridge).

Most of the remaining literature is concerned with dyes of the conventional type having some novelty in the type of nucleus or some modification of the polymethine chain. Thus Homer and Cressmann[37] describe dyes containing a naphtho(1 : 2)selenazole nucleus, and Kendall and Doyle describe sensitizing dyes having a cyano substituent in the chain,[38] and others in which a *cyclo*hexene ring forms part of the chain.[39] Among other publications[40–43] on the preparation of new dyes may be mentioned a patent by Kendall and Edwards[44] on dyes containing only one nucleus with a 3-carbethoxy-3-cyano-2-methylmercapto substituent.

Kainrath[45] has given a useful review and bibliography of advances in sensitizing-dye chemistry up to 1948. He points out that almost all of the useful dyes are of the polymethine type, but very few of the many examples that have been synthesized and tested have satisfactory photographic properties, and no generally valid relations between constitution and sensitizing (as distinct from light-absorbing) properties are known.

Supersensitizers.—Carroll and Spence[46] have patented the use of a quinoline base having an acyloxy group attached to one of the carbon atoms for supersensitizing—that is, enhancing the optical sensitization of—an emulsion sensitized with a cyanine dye. The effect may be accompanied by the development of new long wavelength absorption bands, which are attributed to the conversion of the dye to another state. A Dutch patent[47] describes the use of the thiocyanate of ammonium or a metal as a supersensitizer. A patent by Carroll and Staud[48] and another by Carroll and Brooker[49] describe combinations of a basic dye with a dye of the oxonol series that give a superadditive sensitization.

Chemical sensitizers.—In 1936 Koslowsky of the Agfa Laboratories at Wolfen discovered that a permanent two- to three-fold increase of sensitivity could be obtained by adding to the emulsion, during the after-ripening or before coating, gold complex salts in the form of aqueous solutions of ammonium or alkali aurous thiocyanates. This information became public after the war[50] and stimulated further publications. Mueller[51] now states explicitly that the new materials produced by Ansco at that time, which were some four times faster than the older materials of the same grain size, were prepared by this technique. Other manufacturers, it will be remembered, achieved similar results very shortly afterwards. Mueller considers that the gold is deposited on silver nuclei formed during after-ripening—in fact the gold effect provides the main evidence that such nuclei exist—and points out that this fits in with the fact (reported last year) that a strong latent-image intensification can be obtained by post-fixation gold treatment and physical development. He further supposes that the function of the thiocyanate is to

dissolve the silver halide slightly and lay bare any sub-surface silver nuclei. A recent Dutch patent,[52] however, states that the thiocyanate is best added before after-ripening, and another patent[53] from the same source describes the use of thiocyanates as chemical sensitizers without gold; in these cases the thiocyanate may perhaps be acting as a sulphur-sensitizer. A note by Steigmann[54] states that the gold compounds used for sensitizing are readily reduced by certain substances present in gelatin. Too much of these reducers causes fog, which can be inhibited, however, by conventional anti-fogging agents.

Other heavy metals are employed in a sensitizing process patented by Smith and Trivelli.[55] The emulsion is digested in an acid medium with, for example, a small amount of $(NH_4)_2PtCl_4$ and a larger amount of NaCNS. Lowe and Tarkington[56] describe the use of ethylenediamine for sensitizing emulsions prepared with far-hydrolysed cellulose esters; sulphur-sensitizers such as NH_4CNS give a further sensitization.

Fog inhibitors and stabilizers.—Further patents from Heimbach and Kelly[57–59] deal with the preparation of certain triazaindolizines and related compounds and their use as antifogging agents and stabilizers. Dersch[60] claims that 2 : 3 : 5-triazines inhibit fog without desensitizing and describes the preparation of examples, which, incidentally, also contain mercapto groups. A patent by Dersch and Clark[61] describes the use of tetrazolyl disulphides. Blake[62] claims that the addition of minute amounts of metol, p-$MeNH{\cdot}C_6H_4OH.\frac{1}{2}H_2SO_4$, stabilizes the emulsion against fogging induced by ageing. W. F. Smith and his co-workers have made further claims concerning the use of inorganic compounds of ruthenium, rhenium, and palladium as fog inhibitors.[63,64] In the examples given the ruthenium and rhenium are present in cationic form, the palladium either as a cation or a complex anion, e.g. in $K_2Pd(CNS)_4$. A paper by Taboury and Salvinien[65] contains a discussion of non-colloidal antifogging agents in relation to the fog-inhibiting properties of gelatin.

Miscellaneous addition agents.—A series of war-time studies on organic addition agents for emulsions and developers by Oyama has just come to hand.[66] In the first he gives a classification of these agents, points out that most of them can form salts or double salts with silver ions or salts, and discusses the characteristic groups and linkages that occur, e.g. in sensitizers and in agents giving a blue-black developed image. Most agents have two or more distinct independent actions, e.g. on sensitivity and on image colour. In the second and third he deals with derivatives of mercaptobenzimidazole and related substances and describes their action on fog, rate of development, and image colour. Continuing the studies reported last year, Bycichin and Vlach[67] have examined the anti-fogging and desensitizing action of betaine on unwashed silver bromide–gelatin emulsions.

A patent by Knott and Morgan[68] claims that the deterioration of image colour and reflection density of photographic prints ('bronzing') is decreased by the addition, to the emulsion or one of the processing solutions, of compounds of the type $RSC(NH_2X)NH_2$ where R is an alkyl group, which may contain substituents, and X is a halogen. Compounds which contain the group $NHCOR$, where R is alkyl, and to which a

heterocyclic radical is joined through the N, are said to be particularly beneficial.

A Russian patent of 1947[69] claims that a γ of 12 can be obtained by treating a silver bromide emulsion coating with an aqueous–alcoholic solution of a phenylhydrazine salt of hydrochloric or another acid.

Photographic supports

The properties of cellulose nitrate, cellulose acetate–propionate and high acetyl-content cellulose acetate as motion-picture supports are critically reviewed by Fordyce.[70] Those made from high acetyl-content cellulose acetate are said to approach closely the desirable properties of cellulose nitrate without, of course, its inflammability.

A considerable amount of activity in the field of improved subbings and antihalation layers for films and plates is again apparent during the year. Subbing agents investigated include formamide, and glycerol α-chlorohydrin,[71] aliphatic amides,[72] ascorbic acid,[73] diphenyl sulphones,[74] unsaturated lactones,[75] polyvinyl acetal[76] and heterocyclic nitrogenous bases such as piperidine.[77] Special subs for supports other than cellulose esters, such as methacrylate polymers[78,79] for polyvinyl chloride supports indicate the interest in these low-distortion materials.

A large group of dyes stated to be useful for filter and antihalation dyes is claimed by Thompson[80,81] by reacting pyrilium or benzopyrilium salts containing a reactive methyl group, with aromatic aldehydes. Non-diffusing antihalation 'pigments' have been described which comprise the silver salts of substituted hydroxytriazolopyridazines or pyrimidines.[82] Attention has also been directed towards vehicles for antihalation layers and vinyl pyridine polymers are claimed as superior to gelatin for the purpose.[83] Xanthylium dye salts are suggested as suitable antihalo materials for use in such non-gelatino vehicles.[84] Alkali soluble fractions of guaiacum resin form another type of vehicle.[85] A novel plate backing, comprising alternate stripes of smooth and mat surface area enables the backing to be readily distinguished from the emulsion in total darkness.[86]

The prevention of 'static' on photographic film is the object of two patents, the one[87] employing a gelatin layer washed with an alcoholic alkali metal hydroxide and the other[88] a dialkyl hydrogen phosphate in gelatin, etc. Improved wet-strength papers continue of interest as photographic supports.[89]

Processing

The results of further studies on metol(*N*-methyl-*p*-aminophenol sulphate)–hydroquinone systems have been published by Levenson.[90] To the phenomenon of adsorption of developer to the silver halide is attributed the apparent excess consumption of the former over the theoretical. The 'rate super-additivity' effect, whereby hydroquinone assists the activity of the combined developer, although ineffective on its own, cannot be accounted for on the induction period theory of James. Further evidence is adduced to support the view that the effect is one of metol regeneration. The ability of resorcinol to develop a latent image in solutions of high alkalinity has been demonstrated by James and Levenson.[91]

Continental workers continue to study the influence of redox potentials and p_H on the process of development. In a paper by Jenny,[92] the suggestion that the redox potentials of useful developing agents lie in the range 0·7–0·8 v. is made. By demonstrating that the threshold potential is the same for fog formation and for image development, Abribat, Pouradier and David[93] support the view that development is a kinetic phenomenon. In further studies of the site of reaction in photographic development, James[94] has 'physically developed' the latent image of exposed emulsions by treatment with gold thiocyanate. The gold particles are situated on the surface of the silver halide grain and are 20–80 mμ. in radius. An interesting latensification results from such treatment, which is also described by Mueller.[51] Burton[95] produces a timely paper to demonstrate how development effects may vary throughout the depth of a photographic emulsion and this is added to in a paper by de Vaucouleurs[96] on the effect on optical density of a non-uniform distribution of silver grains within a layer. Further light on developing agents continues to be shed by their consideration as reducing agents in the Landolt reaction, and Eggert[97] shows that very different reaction times are shown by different developers and other agents of photographic interest.

A new class of developing agents is introduced by K. Kumetat[98] based on hydroquinone derivatives in which one ring hydrogen atom is substituted by a pyridinium ring. Certain members of this class are capable of colour development. An unusual function of *iso*-vitamin *C* and of l-adrenaline as photographic reducing agents is described by Rzymkowski.[99] A curious alkaline ferrous-iron developer, used in the absence of oxygen, is described by James[100]: it produces images capable of use as mordants for dyes.

Fine-grain developers now seem to attract comparatively little attention. A quantitative inter-comparison of their properties is published by Ditlevson.[101] A formula for a dry-powder composition containing ethylenediamine sulphate and sodium chloride, which yields a fine-grain developer when dissolved, is claimed by Henn and Crabtree.[102] An interesting statistical examination of the relationship between negative density-scales and the sensitometric exposure-scales of photographic papers results in the abandonment by Jones and Nelson[103] of the term 'useful-exposure scale.'

In the realm of processing methods, Levenson[104] contributes a useful comparison of the initial rates of aerial oxidation of metol–hydroquinone developers during the processing of motion-picture material by immersion and by jet or spray application respectively. Agents to reduce such oxidation are described by Henn.[105] As would be expected, an increase in the speed of fixation was found to result from the use of mixed sodium and ammonium thiosulphates in place of the former alone[106] but otherwise little work seems to have been published on fixation. As a substitute for fixation, stabilization continues to attract attention and Russell[107] patents a mixture of thiourea, acetic acid and gold chloride which is claimed to stabilize a developed image against high temperatures and humidities. A combined silver and dye image on photographic printing paper is described by Dimsdale[108] with the object of conserving silver.

Suitable mercuric chloride intensifiers for use with modern high-speed materials are described by Willcock.[109] The toxicity of metalloids and organic metal compounds used in photography is considered by Schoofs.[110]

New materials and processes

An entirely new non-silver photographic printing process, under the name 'xerography'[111,112] makes use of a metal plate coated with a thin layer of photoconductive material. The plate is sensitized by the application of a uniform static charge, and is discharged image-wise by exposure to light through a positive. On dusting the exposed plate with a finely powdered fusible pigment, the powder adheres to the charged image. This powder image is then transferred, by electrostatic attraction, to a charged paper sheet, and fixed by heating. The plate is then completely discharged and is ready for re-use. Photomechanical applications of this process are discussed in the 1950 'Penrose Annual.'

Rott[113] continues to work on the reversal–transfer type of process, and describes a modification in which the silver salts in the sensitive layer diffuse into a second gelatin layer containing traces of an inorganic colloidal material which assist their development. Applications to the Transargo process (positive direct document copies), the one-step (e.g. the Land) camera, the Diaversal process and the contourfilm (*see* 1948 Report) are discussed. The Diaversal process is described in detail by B. Meerkämper.[114]

The Corning photosensitive glasses have been studied in detail as to their basic composition, light-absorption properties and reaction to heat, by S. Stookey[115]; McKay[116] describes the use of these glasses in the production of permanent photographs.

What has long proved a troublesome property of photographic materials —their sensitivity to pressure—is turned to good account in a method by which they are caused to reproduce surface contours pressed against them.[117]

An interesting application of the differing properties of internal and external latent images is patented by Knott and Stevens.[118] A single support carries two superimposed sensitive layers, one of which, on exposure, gives internal and the other external latent images; either emulsion may be exposed and developed separately. A multicontrast material, prepared by mixing a spectrally sensitized silver halide emulsion with the same emulsion unsensitized, and exposing through suitable filters is patented by Carroll,[119] and a dry developing negative material, consisting of a mercuric salt, sensitized with ferric oxalate and developed by ammonia gas is described by Slifkin.[120]

Materials with overcoatings of removable resins have been described, in the one case to provide a stable wet-printing paper[121,122] and in the other, to provide an X-ray film protected from the action of visible light.[123]

An improved parallax panoramagram, with increased illumination of the image, is claimed by Bonnet.[124] Steady progress in high-speed photography continues to be made: probably the most spectacular is the Zarem camera operating at ten million exposures per second.[125] The shutter is an electro-optical Kerr cell.

Colour photography

Once again the year's main activity appears to have been in the field of new developing and coupling agents, with particular reference to the monopack subtractive process; there are no basic advances to report. The most interesting material is the colour-release positive stock, based on the patents of Jennings, Murray and White (*see* 1948 Report) in which the gelatin of the multilayers is replaced by a synthetic polymer which, besides acting as a vehicle for the silver halide, is itself a colour coupler; this material is described by Sease.[126] A new principle of colour development has been described by Rzymkowski,[127] in which titanium dioxide is formed image-wise with the silver during development and acts as a mordant for a dye contained in the developing solution. The silver image is later removed. Methods of reversing emulsion layers inaccessible to light, such as treatment with X-rays, γ-rays or supersonic vibrations have been patented by Gross.[128]

Among the developing agents, hydrazines[129] and hydrazones[130] are suggested in patents. Many patents on coupling agents have appeared; they include those based on *p*-hydroxybenzyl alcohol,[131] phthalidene-acetamides,[132] 1-naphthol-2-carboxamide,[133] alkoxypyrazolones,[134] *N*-substituted J acids,[135] substituted open-chain keto–methylene compounds,[136] diacyl hydrazides or hydrazones[137] and others. The object aimed at in such work is, in the main, the final production of non-wandering dyestuffs, although a patent by Zeh, Schneider and Frölich[138] also claims non-bronzing as among the virtues of phenylpyrazolone couplers. A useful guide to this maze of compounds is provided in a review article on colour development in the presence of couplers, by Merckx.[139] The integral masking system, in which coloured couplers are employed which change colour at those points at which development occurs, giving a coloured image on a differently coloured background, calls for special coupling agents: such materials, based on *p*-hydroxyazophenolic compounds, are patented by Glass, Vittum and Weissberger.[140] A description of the use of such masks and a discussion from the theoretical standpoint occurs in a paper by Miller.[141] Suitable filter layers for use in monopack multilayer materials are described by Duerr, Morreall and Harsh[142]; they consist in combining the action of a colloidal silver layer with the addition of a yellow azo dye to the magenta layer and a red azo dye to the cyan layer. The production of improved colloidal silver filter layers by deposition on colloidal silver sulphide or selenide nuclei is claimed by Dickinson.[143]

In the field of the silver dye-bleach process, a new group of monoazo compounds, containing a thiazolone cyanine component, has been patented by Thompson,[144] and a series of blue-green dyes suitable for the imbibition process is claimed in a British patent.[145] Dugromacolor—yet another additive process for motion pictures, using a multilens system claimed to be free from parallax,—forms the subject of papers by Blemmec[146] and Thevenet.[147]

A bipack film with a stripping layer is described by Jennings[148] in which positive controlled stripping from an intermediate polyvinyl acetal layer is claimed. A curious combination of hand and photographic work is described in a patent by Hoff,[149] in which a black and white negative is

hand-coloured with complementary colours and printed on to a suitable photographic colour-printing paper.

Problems relating to the exposure of colour film are dealt with in a paper by Harrison,[150] and a detailed scheme for the analysis of developers and bleaches used for Ansco colour film is given by Brunner, Means and Zappert.[151]

Photomechanical processes.—The emphasis during the year has been on new materials and processes, although a useful discussion of basic factors affecting the adherence of photomechanical layers to their bases has been given by Smethurst[152]; Cartwright[153] and Caldwell[154] describe respectively the nature of the diffusion of ferric chloride solutions in photogravure and the importance of temperature control in still etching. Three papers by Mackenzie[155,156,157] review the possibilities and limitation of the silk-screen process. An important contribution to photolithography refers to printing plates formed from surface-hydrolysed cellulose esters[158] in which differentially hardened images are produced by dichromate sensitization. Alternatively, a cellulose ester may carry a silver halide emulsion which, on conversion to a stencil, may be used to control the hydrolysis of the underlying cellulose-ester support. A new sensitizer-medium for lithographic plates, consisting of an alkaline mixture of casein and gelatin, is patented by Buck and Miller,[159] and a preservative for paper or plastic litho plates, of gum acacia, potash alum and sodium sulphite, by Osinski and Bucklin.[160]

An increase in range of tones is claimed for a photogravure process in which the area and depth of the ink cells, rather than their number, are varied.[161] Attention is still being given to the problem of photogravure for all-over cylinder designs.[162] The simultaneous etching of picture and type matter is described by Wolfson,[163] using a special double-coated process film. The top layer is partially colour-developed and forms an actinic-ray blocking-screen for the picture part.

The production of sharply defined stencils in shellac or phenol–formaldehyde resins is described in a process patented by Gresham and Loening[164] by the image-wise etching of these resists through a superimposed light-sensitive layer which is itself etched image-wise. The resultant composite stencil may be used for glass etching, for electroplating surfaces for lithography and for other purposes. An interesting method of producing half-tone gelatin printing plates by the use of a lenticular screen to produce hardened dots on the sensitized layer has been patented by Ernst.[165] A form of drop-out process, described as 'perfect,' uses a glass half-tone screen with magenta cross-lines.[166] A novel copper printing plate is described by Terry,[167] which is prepared by electrodeposition on a wax pressing from a grained carrier, the graining of which has been modified by a thin gelatin–silver halide emulsion, exposed and tan-developed. Colour separation methods for reproducing colour originals are claimed to be facilitated by using fluorescent substances in the original, and copying in ultra-violet light.[168]

Diazo and blue-print

An excellent general review outlining the principles of diazotype printing, the preparation of suitable materials and the possibility of

extending such processes to colour photography is given by Delattre[169]; Slifkin[170] goes on to describe colour applications with Ozachrome. Research into the diazo processes continues at a steady pace; attention is mainly divided between the stabilization of existing diazo processes and the production of substituted diazo materials giving greater visual and photographic density. Agents to obtain stability include additions of sulphonated hydroxycarboxybenzene or naphthalene[171] and the use of resorcinol carbonamides.[172] A novel stabilization method involves the preparation of diazo-sulphonated resins, such as diazotized formaldehyde-naphthalene sulphonic acid salts, which are light-sensitive.[173] Johnston[174] continues work on benzyloxy and acylamino substituents in diazotized aromatic rings and claims prints of dark colour and high contrast. The preparation of derivatives of aryl diazo sulphones, suitable as light sensitive elements, has been described.[175] Greater printing latitude is claimed from the addition of ascorbic acid to diazo coating compositions[176] —yet another advantage of vitamins—and advantages in the low-temperature drying of heavy layers of sensitizing material are said to result from the use of cellulose ethers as addition agents or as paper sizes.[177] Improved diazo materials for screen reflectography are claimed in a Dutch patent,[178] and photosensitive cloths for the ferroprussiate, diazo or sepia processes are described by Norman.[179]

There would appear to be little recorded work on blue prints; an alkaline marking-composition of high stability, having a vehicle of hydroxyethyl cellulose has been patented by Fisher.[180]

References

[1] Mitchell, *Phil. Mag.*, 1949, **4D**, 249
[1a] Stasiw and Teltow, *Nachr. Ges. Wiss. Göttingen, Math. Phys.*, 1941 [K1], 93, 100, 110; 1947 [K1], 155; *Ann. Phys.*, 1941, **40**(5), 181; 1947, **1**(6), 261; *Z. anorg. Chem.*, 1948, **257**, 103, 109
[2] Meidinger, *Z. wiss. Photogr.*, 1949, **44**, 1
[3] Idem, *Sci. Ind. Photogr.*, 1949, **20**, 321
[4] Berg, ibid., 401
[5] Vanselow, Quirk, and Leermakers, *PSA J.* **14**, 675, 1948
[6] Berg and Ford, *Photogr. J.*, 1949, **89B**, 31
[7] Arens, *Z. wiss. Photogr.*, 1949, **44**, 44, 172,
[8] Annual Reports, 1947, **32**
[9] Kornfeld, *J. opt. Soc. Amer.*, 1949, **39**, 490
[10] Sauvenier and Winand, *Bull. Soc. roy. Sci., Liège*, 1949, **18**, 156
[11] Hautot and Sauvenier, *Sci. Ind. Photogr.*, 1949, **20**, 286
[12] Meidinger, *Z. wiss. Photogr.*, 1949, **44**, 137
[13] Vassy, Schonne and Vassy, *C.R. Acad. Sci., Paris*, 1947, **224**, 910
[14] Vassy and Vassy, ibid., **225**, 55
[15] Farnell and Pinoir, *Sci. Ind. Photogr.*, 1949, **20**, 205
[16] Berriman, *Photogr. J.*, 1949, **89B**, 121
[17] Webb, *Phys. Rev.*, 1948, **74**, 511
[18] Berriman, *Nature*, 1948, **162**, 992
[19] Herz, *Photogr. J.*, 1949, **89B**, 89
[20] Albouy and Faraggi, *J. Phys. Radium*, 1949, **10**, 105; Faraggi and Albouy, *Sci. Ind. Photogr.*, 1949, **20**, 336
[21] Ammann-Brass, *Kolloidzschr.*, 1948, **110**, 1, 105 and 161; *Sci. Ind. Photogr.*, **19**, 1948, 401 and 1949, **20**, 441
[22] Steigmann, *Sci. Ind. Photogr.*, 1949, **20**, 284
[23] Damschroder and Kauffman, U.S.P. 2,449, 980
[24] Pouradier and Abribat, *Sci. Ind. Photogr.*, 1949, **20**, 444
[25] Lowe, U.S.P. 2,455,936

[26] Idem, U.S.P. 2,455,937
[27] Staehle, U.S.P. 2,439,108
[28] Barnes and Ney, U.S.P. 2,461,023
[29] Sauvenier, *Sci. Ind. Photogr.*, 1949, **20**, 48
[30] Idem, ibid., 41
[31] Hamer, Rathbone, and Winton, *J. chem. Soc.*, **1948**, 1872
[32] Anish, U.S.P. 2,450,390
[33] Wilson, U.S.P. 2,465,412
[34] Brooker, U.S.P. 2,461,137
[35] Schwarz and de Smet, B.P. 615,205
[36] Fr. Pat. 930,514
[37] Homer and Cressman, B.P. 610,566
[38] Kendall and Doyle, U.S.P. 2,471,488
[39] Idem., B.P. 604,217
[40] Hamer and Knott, B.P. 593,023
[41] Kendall, Suggate and Wood, U.S.P. 2,474,426
[42] Hamer, *J. chem. Soc.*, **1949**, 32
[43] Knott, U.S.P. 2,469,830
[44] Kendall and Edwards, B.P. 610,569
[45] Kainrath, *Angew. Chem.*, 1948, **60A**, 36
[46] Carroll and Spence, U.S.P. 2,450,748
[47] Kodak, N. V., Dutch Pat. 62,394
[48] Carroll and Staud, U.S.P. 2,448,858
[49] Carroll and Brooker, U.S.P. 2,432,468
[50] Koslowsky and Mueller, Agfa Film Plant Reports, Sep.–Oct. 1936; Bibliogr. sc. and indust. Reports (U.S. Dept. of Commerce), **8**, 873; P.B. 70,053; *see also Sci. ind. Photogr.*, 1948, **19**, 189
[51] Mueller, *J. opt. Soc. Amer.*, 1949, **39**, 494; *Sci. Ind. Photogr.*, 1949, **20**, 281
[52] Kodak N.V. Dutch Pat. 62,396
[53] Idem. Dutch Pat. 62,395
[54] Steigmann, *Brit. J. Photogr.*, 1949, **96**, 223
[55] Smith and Trivelli, U.S.P. 2,448, 060
[56] Lowe and Tarkington, U.S.P. 2,448,534
[57] Heimbach, U.S.P. 2,450,397
[58] Heimbach and Kelly, U.S.P. 2,449,225
[59] Idem, B.P. 623,116
[60] Dersch, U.S.P. 2,476,536
[61] Dersch and Clark, U.S.P. 2,465,149
[62] Blake, U.S.P. 2,449,836
[63] Stauffer and Smith, U.S.P. 2,458,442
[64] Smith and Trivelli, U.S.P. 2,472,626
[65] Taboury and Salvinien, Recherche aeronaut. (O.N.E.R.A.), 1948, 47
[66] Oyama Yasushi, *Bull. Inst. phys. chem. Res., Tokyo*, 1942, **21**, 364; 1943, **22**, 483; 1944, **23**, 23
[67] Bycichin and Vlach, *Chem. Listy*, 1948, **42**, 56; *Sci. Ind. Photogr.*, 1948, **19**, 263
[68] Knott and Morgan, U.S.P. 2,461,987
[69] Bukatin, U.S.S.R. Pat. 67,873
[70] Fordyce, *J. Soc. Motion Pict. Engrs.*, 1948, **51**, 331
[71] Kaszuba, U.S.P. 2,461,472
[72] Idem, U.S.P. 2,461,473
[73] Idem, U.S.P. 2,461,475
[74] Idem, U.S.P. 2,461,474
[75] Idem, U.S.P. 2,461,476–77
[76] Woodward, U.S.P. 2,462,151
[77] Easton, U.S.P. 2,461,467
[78] Hart and Lee, B.P. 573,917
[79] Beguin and Swan, U.S.P. 2,388,817
[80] Thompson, U.S.P. 2,461,484
[81] Idem, B.P. 615,252
[82] Heimbach, U.S.P. 2,390,707
[83] McQueen and Weaver, U.S.P. 2,448,542; Alles, U.S.P. 2,448,507–8
[84] Thompson, B.P. 611,556

[85] Barrett, Howe and Alford, B.P. 615,120
[86] Janus, Ray and Hance, B.P. 613,134
[87] Famulener, U.S.P. 2,476,240
[88] Mueller, B.P. 617,569
[89] Boughton, U.S.P. 2,394,289
[90] Levenson, *Photogr. J.*, 1949, **89B**, 2, 13
[91] James and Levenson, *PSA J.*, 1949, **15**, 136
[92] Jenny, *Helv. chim. Acta*, 1949, **32**, 315
[93] Abribat, Pouradier and David, *Sci. Ind. Photogr.*, 1949, **20**, 121
[94] James, *J. Colloid Sci.*, 1948, **3**, 447
[95] Burton, *Photogr. J.*, 1949, **89B**, 41
[96] de Vaucouleurs, *Rev. optique*, 1948, **27**, 541
[97] Eggert, *Helv. chim. Acta*, 1949, **32**, 692
[98] Kumetat, *Z. wiss. Phot.*, 1948, **43**, 113
[99] Rzymkowski, *Sci. Ind. Photogr.*, 1949, **20**, 257
[100] James, U.S.P. 2,453,323
[101] Ditlevsen, *Amateur Photographer*, 1949, **99**, 182, 203
[102] Henn and Crabtree, U.S.P. 2,466,423
[103] Jones and Nelson, *J. opt. Soc. Amer.*, 1948, **38**, 897
[104] Levenson, *Brit. Kinematography*, 1949, **14**, 65
[105] Henn, U.S.P. 2,458,376
[106] Ingraham, U.S.P. 2,475,616
[107] Russell, U.S.P. 2,453,346
[108] Dimsdale, B.P. 614,808
[109] Willcock, *Brit. J. Photogr.*, 1949, **96**, 39
[110] Schoofs, *Photographer*, 1948, No. 680, 295
[111] Schaffert and Oughton, *J. opt. Soc. Amer.*, 1948, **38**, 991
[112] Wilson, *U.S. Camera*, 1948, **11**, 46
[113] Rott, *Tech. Wetensch., Tijdschr.*, 1948, **17**, 163
[114] Meerkämper, *Camera (Lucerne)*, 1949, **28**, 113
[115] Stookey, *Ind. Eng. Chem.*, 1949, **41**, 856
[116] McKay, *Amer. Photogr.*, 1948, **42**, 40; *Bull. Brit. sci. Instrum. Res. Ass.*, 1948, **3**, 281
[117] Mather, *J. opt. Soc. Amer.*, 1948, **38**, 1065
[118] Knott and Stevens, U.S.P. 2,452,765
[119] Carroll, U.S.P. 2,384,598
[120] Slifkin, U.S.P. 2,459,136
[121] Minsk, Weyerts and McDowell, U.S.P. 2,391,181
[122] Welford, U.S.P. 2,452,705
[123] Murray, U.S.P. 2,462,534
[124] Bonnet, B.P. 615,629
[125] *Electronics*, 1948, **21**, 92
[126] Sease, *Amer. Cinematog.*, 1949, **30**, 240, 257
[127] Rzymkowski, *Fotografie*, 1948, **1**, 63; *Sci. Ind. Photogr.*, 1948, **19**, 426
[128] Gross, Canad. Pat. 452,990
[129] Hanford, B.P. 608,520
[130] Kendall and Suggate, U.S.P. 2,449,388
[131] Vittum and Weissberger, U.S.P. 2,476,008
[132] Leekley, U.S.P. 2,472,666
[133] Weissberger, Salminen and Vittum, U.S.P. 2,474,293
[134] Gregory, U.S.P. 2,472,581
[135] Tulagin, U.S.P. 2,445,252
[136] Weissberger and Porter, U.S.P. 2,439,352
[137] Gevaert, B.P. 615, 447
[138] Zeh, Schneider and Frölich, U.S.P. 2,437,063
[139] Merckx, *Sci. Ind. Photogr.*, 1949, **20**, 1
[140] Glass, Vittum and Weissberger, U.S.P. 2,455,169 and U.S.P. 2,453,661
[141] Miller, *J. Soc. Mot. Pict. Engrs.*, 1949, **52**, 133
[142] Duerr, Morreall and Harsh, U.S.P. 2,464,798
[143] Dickinson, B.P. 619,283
[144] Thompson, U.S.P. 2,464,785
[145] Technicolor, B.P. 607,792
[146] Blemmec, *Le Cinéopse*, 1949, **25**, 4

[147] Thevenet, *Le Photographe*, 1949, **39**, 53
[148] Jennings, U.S.P. 2,462,503
[149] Hoff, U.S.P. 2,461,469
[150] Harrison, *Photogr. J.*, 1949, **89A**, 16
[151] Brunner, Means and Zappert, *J. Soc. Mot. Pic. Engrs.*, 1949, **53**, 25
[152] Smethurst, *Process Engrav. Mon.*, 1947, **54**, 170, 173, 198, 201
[153] Cartwright, ibid., 1949, **56**, 45–46
[154] Caldwell, *Photo-Engrav. Bull.*, 1948, **38**, 76–81
[155] Mackenzie, *Process Engrav. Mon.*, 1947, **54**, 86, 89, 114, 117
[156] Idem, ibid., 254, 257
[157] Idem, *J. Text. Inst., Manchr.*, 1948, **39**, A 534
[158] Colt, U.S.P. 2,448,861
[159] Buck and Miller, U.S.P. 2,387,056
[160] Osinski and Bucklin, U.S.P. 2,463,554
[161] Schultz, Nestle and Romano, U.S.P. 2,431,710
[162] Cartwright, *Process Engrav. Mon.*, 1947, **54**, 289
[163] Wolfson, U.S.P. 2,431,359
[164] Gresham and Loening, U.S.P. 2,459,129
[165] Ernst, U.S.P. 2,430,498
[166] Grady, *Photo-Engrav. Bull.*, 1946, **36**, 63
[167] Terry, U.S.P. 2,462,570
[168] Switzer, U.S.P. 2,434,019
[169] Delattre, *Chim. et Industr.*, 1948, **60**, 233
[170] Slifkin, *Modern Lithography*, 1949, **17**, 36, 99
[171] Reichel, B.P. 617,451
[172] Neumann, U.S.P. 2,467,358
[173] General Aniline and Film Corpn., B.P. 615,685
[174] Johnston, U.S.P. 2,456,514
[175] Sprung and Schmidt, U.S.P. 2,465,760
[176] Botkin and Slifkin, U.S.P. 2,465,424
[177] Slifkin, U.S.P. 2,474,700
[178] van der Grinten, Dutch Pat. 62,005
[179] Norman, B.P. 573, 975
[180] Fisher, U.S.P. 2,466,799

FATS, FATTY OILS AND DETERGENTS

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THE continued world shortage of oils and fats makes it more than ever necessary that methods of processing and of utilization should be subjected to searching scrutiny with a view to the introduction of new methods and the improvement of existing ones: available fat resources should be used to the best possible advantage. Many new processes have been reported during the last few years, such as the fractionation of fats by selective extraction, the modification of fats by such methods as inter-esterification, new methods of refining by continuous processes and the continuous production of soap. In due course, such processes will undoubtedly revolutionize the oil and fat industry, resulting in greater economy of production and in the availability of new types of fatty glycerides not obtainable from natural sources.

The present year appears to have been a period of consolidation: it has not been marked by the appearance of any work of outstanding significance or novelty, although there has been a steady stream of publications, largely from American sources. A continued interest has been shown in detergents and in methods for evaluating their efficiency, reflecting not only the importance and the complexity of the subject but also the need for further fundamental work into the problems involved.

This report will follow the lines adopted last year and will be confined to a discussion of selected papers considered to be of general interest. A detailed review of the literature, involving numerous references to matter of importance only to the expert, has not been attempted.

Oil seeds

The curing and storage of oil-bearing seed is of such importance that data regarding the hygroscopic equilibrium of the seed and the rate of attainment of the equilibrium is of considerable interest. This information has now been reported for groundnuts at 25° C. in atmospheres of relative humidity ranging from 11–92½%. In general, the time taken to attain equilibrium was dependent on the initial moisture content of the nuts, but equilibrium was always reached within 10 days except for freshly-dug groundnuts at the three highest relative humidities (75½, 86½ and 92½%). The corresponding moisture contents of the seed at these humidities were 10½, 13½ and 20%. The method of curing did not appear to affect the equilibrium moisture contents.[1] An investigation has been made into the effect of the cooking of cottonseed 'meats' on the bleached colour of the refined, screw-pressed oil and on its storage properties. It was shown in laboratory tests that the addition of about 10% of water to the flaked 'meats,' before cooking at 240° F., improved the colour of the bleached oil. In a factory experiment this conclusion was not confirmed, but it was found that the oil maintained its colour during storage much better than oils from the dry-cooked seed.[2]

Processing of oils and fats

Bleaching.—During the adsorption bleaching of vegetable oils, chemical reactions such as oxidation are also involved and the final colour represents the net result of a number of factors, some of which are favourable to the process whereas others are not. Some oils increase and others decrease in colour when they are heated in air, but in both cases the oxidation stabilizes the colour against adsorption. A comparison has been made between atmospheric and vacuum bleaching with activated clays and it was found that for both types of oil significantly lower colours result when bleaching is carried out under vacuum or in an inert atmosphere. Low-p_H clays responded better than those with a high p_H as regards both colour improvement and the resistance of the bleached oil to oxidation.[3] On the basis of this laboratory work a vacuum bleaching system has been designed in which a slurry of oil and adsorbent is first sprayed into a vacuum chamber at 130° F., to effect de-aeration and dehydration of the mixture. The slurry is then pumped through a heat exchanger and sprayed at 230° F., into a second vacuum chamber. The process, which is continuous, has been in operation for a number of years and is claimed to result in economy in the use of adsorbent. Lower colours are obtained in the vacuum bleached oils which have better stability to oxidation and to flavour reversion.[4]

Selective extraction.—A description has been given of the Solexol process using liquid propane for the counter-current extraction and refining of oils. The process can be applied not only to the fractionation of oils such as soya bean, linseed, fish oils and tall oils, but it can also be used for the isolation of vitamin and sterol concentrates and as a simple refining process for the removal of colour and fatty acids. The crude oil enters the middle of an extraction tower and the propane, under sufficient pressure to keep it liquid at the operating temperature, enters at a point near the bottom. The temperature is regulated so that a desired proportion of the oil is dissolved in the propane while the remainder falls to the bottom of the tower as an insoluble phase. In this way as small a fraction as 1% can be removed in which the colour and the oxidized impurities are concentrated, and a refined product is obtained from the top of the tower. This product may be re-fractionated in a second tower to give two fractions of different unsaturation or it may be fractionated so that the greater part of the oil is removed from the bottom of the column while a small vitamin or sterol concentrate is taken from the top. The latter fraction will also contain the greater part of the free fatty acids and when the primary consideration is the quality of the vitamin concentrate, it is preferred to neutralize the crude oil with caustic soda before it is subjected to the fractionation processes.

The size of the fractions obtained is regulated by the temperature of operation, a higher temperature resulting in a larger bottom fraction. This is of course contrary to the temperature effect usually obtained in extraction processes and the explanation lies in the fact that the propane is being used at temperatures approaching the critical temperature (206° F.). As the temperature is varied in this region, there will be marked changes in the density of the liquid propane with corresponding

changes in its solvent power. If, therefore, the temperature at the top of an extraction tower is maintained at, say, 170° F., and the temperature of the incoming propane is 150° F., the temperature gradient will cause such changes in the density of the propane that its solvent effect will decrease considerably from the bottom to the top of the tower. In this way an internal 'reflux' is maintained, additional insoluble phases separating from the propane at the higher points in the tower and falling back to a lower level where they are redissolved by propane of higher density. It should be noted also that the insoluble bottom fraction is the more unsaturated of the two.

The fractionation of cod liver oil and of soya bean oil may be cited as typical applications of the Solexol process. The cod liver oil (previously neutralized) is treated continuously in two extraction towers and a 25% fraction having an iodine number of 210 is obtained from the bottom of the first tower; a 70·5% fraction (iodine number 155) is obtained from the bottom of the second column and a 4·5% concentrate containing 41,000 units of vitamin *A* per g. is drawn from the top. With soya bean oil, using three extractors, four fractions are obtained, namely, an unsaponifiable concentrate (1%), a fraction of iodine number 128 (72%), a more unsaturated fraction of iodine number 155 (25%) and a 2% fraction containing colour, 'break' materials and a proportion of the fatty acids. The 72% fraction is of edible quality, has an acidity of 0·04% and is stated to have satisfactory stability to oxidation[5].

Deodorization.—A semi-continuous process for the deodorization of edible oils and fats has been described for which a high degree of efficiency is claimed. The oil is processed in relatively small separate portions in trays or pans, five being arranged one above another inside a vacuum chamber. The charge is dropped from one tray to the next after 30 min. and the tray is immediately refilled by the contents of the tray above. Thus there is a continuous progression of oil through the plant, a different stage in the deodorization process being accomplished in each tray. In the first the oil is de-aerated and heated with steam to 320–330° F.; in the second it is heated to the deodorizing temperature of 450–460° F. with Dowtherm vapour; in the third and fourth trays the oil remains for two half-hour periods in which it is deodorized by steam at 125 lb./in^2. pressure; it is then cooled to about 140° F. in the fifth tray and discharged from the plant. Stripping steam is supplied also to trays 1, 2 and 5, largely for purposes of agitation. A number of advantages are gained by using a system of trays inside an outer shell with a free space between the trays and the shell: high vacuum is maintained on the oil surfaces at all stages of the process; the possibility of air leaking into the hot oil is completely eliminated; condensate drains to the bottom of the shell where it cannot contaminate the oil; heat losses are minimized. Since the shell sustains the pressure of the atmosphere the trays and fittings can be of relatively light construction: resistant metal such as nickel need only be used for the trays and the outer shell can be constructed of carbon steel.

The preliminary laboratory investigation of the steam stripping of oil in shallow trays showed that baffles placed a short distance above the oil

surface doubled the efficiency of the deodorizing process. The explanation lies in the fact that the oil is thrown upward and splashed against the baffles by the expanding steam. This method of creating a large interface between the oil and the steam is an important element in the process.[6]

A continuous deodorizer of more conventional type has also been reported in which the oil is treated successively in six chambers, the pressure ranging from 160 mm. mercury in the first to less than 1 mm. in the last. The use of low temperatures, apparently not higher than 80° c., effects a considerable economy in heat consumption and also minimizes the destruction of substances of biological importance.[7]

Hydrogenated fats.—A patented process has been proposed in which 5% of an aqueous solution containing not less than 80% of hydrazine sulphate is mixed with the oil at normal temperature and pressure. The method can be applied to the glycerides of ricinoleic acid and it is claimed that the oil is hydrogenated and deodorized. Excess of the reagent is liberated as ammonia.[8] An investigation into the hydrogenation of castor oil and its fatty acids has been made in order to determine the best method of hardening the oil without affecting the hydroxyl groups. Using a commercial nickel catalyst it was concluded that a temperature of 100–110° c. and a pressure of 100–150 kg. per sq. cm. afforded the best conditions. A product melting at 85–88° c. was obtained.[9]

Two patents concerned with the manufacture of shortening and margarine should be mentioned. A shortening free from bleeding or weeping at ordinary temperatures must contain at least 32% of solid glycerides, but when such a compound is finished by the usual methods it is too hard in consistency for household use. This disadvantage is said to be obviated by cooling the molten fat rapidly to below 10° c. and maintaining it below this temperature until the heat of crystallization is absorbed: the fat may be agitated during cooling. Such a shortening is claimed to have a satisfactory consistency at ordinary temperatures and not to be softened so much by rise in temperature as normal fats finished by the usual methods.[10] A margarine of good consistency and spreading properties is made by dispersing an oil or melted fat in water in the presence of an emulsifying agent, the emulsion being then dispersed in a second oil phase at a temperature below the melting point of the first. The second fat must obviously have the lower melting point of the two. The product is an oil-water-oil emulsion which can be solidified to a plastic margarine.[11]

Esterification and inter-esterification

The reaction between refined groundnut oil and absolute alcohol in the presence of caustic soda as a catalyst has been studied analytically, the course of the reaction being followed by determinations of the amounts of mono-, di- and triglycerides, ethyl esters, glycerol, caustic soda and soap. The solubility of alcohol in groundnut oil at 50° c. was found to be about 31·8% by weight, which is very slightly more than two equivalents. Since this amount of alcohol was not exceeded in any of the experiments

which were mostly carried out at 50° c. the reactants were present in a homogeneous solution. In all the experiments, the reaction proceeded rapidly at first and slowed down quickly after about 15 min., the extent of the reaction depending on the alcohol and catalyst concentrations. For example, 79% alcoholysis was obtained after 20 min. with two equivalents of alcohol and 0·4% sodium hydroxide and after 160 min. the reaction had proceeded to the extent of 99%: the corresponding amounts of free glycerol were 69% and 90% of the maximum amount obtainable. The optimum temperature for the reaction was found to be about 50° c. The rate of soap formation was found to be considerable and to be dependent on the conditions. Consideration of the results obtained in these experiments led to the conclusion that the destruction of the glyceryl ester linkages proceeds in a random fashion during the alcoholysis.[12]

Mixtures of coconut or palm kernel oil with liquid vegetable oils such as groundnut or sunflower oil have been subjected to inter-esterification and, as would be expected, the proportion of fully saturated glycerides in such mixtures was considerably reduced. However, the resulting product was a fat of better texture and consistency with a smaller plastic range.[13] Similar work has been carried out on mixtures of linseed oil with other oils such as sunflower and rapeseed oils. Reaction at 200° c. was found to be most favourable as regards the drying properties of the products, some of which were substantially equal to pure linseed oil. The best results were obtained with calcium naphthenate as catalyst.[14]

Further work has been reported on the so-called directed inter-esterification of fats, in which the formation of a greater proportion of saturated glycerides is induced by allowing them to crystallize from the mixture during the course of the reaction. The catalyst for this process (sodium methoxide in xylene) is also an active catalyst for the reaction between glycerol and triglyceride: therefore, inter-esterification occurred simultaneously with the formation of mono- and di-glycerides when a mixture of cottonseed oil and glycerol was allowed to react. By conducting the reaction at low temperatures (e.g. 10° c.) preferential separation of the saturated acids as mono- and di-glycerides was successfully accomplished and in this way the high-melting and low-melting fatty acids of a fat could be almost completely separated. When the proportion of glycerol and the conditions of the reaction were varied, the separated products could be controlled so that in favourable circumstances either the mono- or di-glyceride was produced in fairly pure condition. Recrystallization of the products obtained from cottonseed oil yielded almost pure samples of mono- and di-palmitin.[15]

A process has been patented for the manufacture of monoglycerides by the continuous counter-current interaction of glycerol (containing 5–10% water) with animal or vegetable oils and fats. Glycerol containing the water is fed into a point near the top of a reaction tower, which is maintained at a temperature of 250° c. and a pressure of 670 lb./in^2. and the oil or fat enters at a point near the bottom. The product is stated to contain 56% monoglyceride and 12·7% free fatty acids: excess of glycerol is removed from the bottom of the tower.[16]

Rancidity and flavour reversion

Methyl oleate has been oxidized in the presence of ultra-violet light and the hydroperoxide was then separated and examined. It was converted to methyl hydroxyoleate and then to methyl hydroxystearate. On oxidation with chromic anhydride in acetic acid, four isomeric keto-stearic acids were obtained with the carbonyl group in the 8, 9, 10 and 11 positions. The methyl hydroxyoleate was also reacted with performic acid to give a mixture of methyl trihydroxystearates which on further oxidation with periodic acid gave suberic and azelaic acids derived respectively from the 8 : 9 : 10- and 9 : 10 : 11-trihydroxystearates. The acid residues from the performic acid hydroxylation were shown to contain suberic, azelaic and sebacic acids. These investigations afford further evidence in favour of the theory that a double-bond shift occurs during the hydroperoxidation reaction, giving rise to four isomeric hydroperoxides.[17] The autoxidation of methyl linoleate at 30° C. has also been investigated. The non-conjugated 9 : 12-ester was oxidized almost three times as readily as the conjugated 10 : 12-ester and by a different mechanism. The whole of the oxygen used in the early stages of the reaction could be accounted for as peroxide oxygen whereas no peroxide was detected until the oxidation of the conjugated ester had proceeded for a considerable time. In the reaction with the 10 : 12-ester, the amount of oxygen taken up was equivalent to the disappearance of the conjugated double bonds, and this suggests a carbon to oxygen mechanism for the polymerization reaction. During oxidation of the 9 : 12-ester there was at first a considerable increase in conjugation (followed by a decrease) and it was concluded that oxygen in the form of hydroperoxide is as powerful as alkali hydroxide in the promotion of conjugation.[18] Concentrates of the hydroperoxides formed by the oxidation of methyl linoleate have been prepared and the hydroperoxide groups were then reduced by means of potassium iodide in chloroform–acetic acid solution. The reduced product had a higher iodine number (equivalent to 2·12 double bonds) than the original concentrate. Using *cyclo*hexanol as the solvent, cryoscopic determinations of the molecular weights indicate without doubt that the original ester, the hydroperoxide concentrate and the reduced concentrate were all monomeric products. The molecular absorption at 2325 A. was 22,700 for the original concentrate and 23,900 after reduction. It was concluded therefore that the initial products of peroxidation are mostly monomeric conjugated monohydro-peroxides.[19]

A polarographic study has been made of the peroxides formed during the autoxidation of fats, the electrolytes used being either lithium chloride or lithium methoxide solutions in a mixture of benzene and methyl alcohol. Three waves were obtained in the current–voltage curves and it was concluded that at least three different peroxide structures were present. The height of the largest of these waves (the other two were small) was found to be proportional to the peroxide value in the early stages of the autoxidation until a peroxide value of about 250 was reached. The current-voltage curves given by lard oxidized at 100° C. were different from those obtained when the oxidation was effected at 45° C.[20]

Analytical examination has been made of the changes occurring in Indian buffalo ghee and Indian cow butterfat after exposure to the atmosphere in loosely corked containers for 3–4 years in diffused daylight. It was noted that the increase in acidity was roughly parallel to the decrease in the iodine number. The Polenske value showed particularly marked increases but after removal of the free fatty acids it was found that both the Reichert and the Polenske values were roughly the same as those of the original fats. The free fatty acids were separated and examined. The normal homologous acids from butyric to capric acid were found in roughly equal amounts (viz. about 8 moles %). Azelaic and palmitic acids were present to the extent of about 10 moles % but no appreciable amount of oleic acid was found. Small amounts of unidentified acids of lower molecular weight than oleic were present as well as non-volatile residues of low iodine number and low equivalent weight—apparently products of polymerization. In spite of wide variation in the composition of the original fats the composition of the free fatty acids was roughly the same in all cases.[21] The nature of the fatty acids formed by lipolytic rancidity (again in ghee butterfat) has also been investigated. The rancid fat contained 13·1% of free acids which consisted of butyric (4·5%), caprylic (0·8%), capric (1·7%), lauric (2·4%), myristic (9·6%), palmitic (11·7%), stearic (8·4%), arachidic (2·1%), oleic (50·4%) and other unsaturated acids (8·4%). The component fatty acids of the original fat (iodine number 29·6) were normal but the neutralized rancid fat contained a much higher proportion of saturated acids. Its iodine number was 21·4.[22]

Work on the spoilage of animal fats exposed in beakers in diffuse daylight for about 2½ years has suggested that as much as 30% of the fat was concerned in the autoxidation process. Epihydrinaldehyde was present to the extent of 1% in one of the samples examined but it did not contribute to the oxidized flavour. It was concluded that linoleic acid is oxidized before oleic and that the 12 : 13 double bond, farthest from the carboxyl group, is preferentially attacked.[23] Similar experiments with groundnut oil led to the same conclusion that oxidation of the glycerides was mostly at the expense of the linoleic acid. Polymerization and an increase in the amount of conjugation were observed. In the later stages of the oxidation an increase in viscosity occurred without a corresponding decrease in the iodine number or increase in the peroxide value. This was interpreted as being due to *cis–trans* isomerization of unsaturated acids leading to the formation of three-dimensional polymers.[24]

It will be recalled that 2-undecenal has been detected in the decomposition products of methyl oleate hydroperoxide. The same investigators have now examined the steam-volatile autoxidation products of cottonseed oil and have demonstrated the presence of 2 : 4-decadienal, 2-octenal and hexanal.[25]

The antioxidant properties of butylated hydroxyanisole have been investigated and the results of laboratory tests with lard have been confirmed by keeping experiments at room temperatures : baking tests showed that the antioxidant properties were carried over into the baked products. Extensive tests on rats have failed to disclose any harmful physiological effects and the use of butylated hydroxyanisole is now

permitted in edible products by the U.S. authorities.[26] The stabilization of vitamin *A* in crude halibut liver oil with nordihydroguaiaretic acid has shown the effect to be much greater at 25° C. than had been indicated by accelerated tests at the temperature of the Swift stability test. At this temperature there was no true induction period either for peroxide formation or for loss of vitamin *A*, whereas at 25° C. an induction period was clearly defined. When 0·1% nordihydroguaiaretic acid was used with 0·1% citric acid as a synergist, the protection factor for 50% loss of vitamin *A* at 25° C. was greater than 28 but at the higher temperature it was not more than 2.[27] It has been stated that the addition of nordihydroguaiaretic acid to lard resulted in no significant increase in the keeping properties of army ration biscuits.[28] Di-*iso*eugenol has been patented as an antioxidant; it is claimed to be superior to nordihydroguaiaretic acid and much better than *iso*eugenol.[29]

Flavour reversion.—Attention has been drawn to the fact that more than one phenomenon has been described as flavour reversion, and that this probably explains to some extent the confusion and lack of agreement between the results obtained by different workers in this field. Work has now been published which suggests quite convincingly that the heat reversion of hydrogenated soya bean oil is not caused by phospholipids or other non-glyceride substances removed by water-washing. Experiments designed to investigate the role of the unsaponifiable matter failed to give definite results: it was found that although hydrogenated cottonseed oil developed a foreign flavour and odour after incorporating the unsaponifiable matter of soya bean oil the typical reverted flavour was not obtained.[30]

The flavour stability of soya bean oil is improved by the inclusion of a small amount (0·01%) of citric acid during the deodorization process and it has been shown that the stability to oxidation of the oil is also improved. The citric acid is destroyed during the deodorization and a further quantity of the acid should be added to ensure subsequent protection of the oil. Phosphatides have also been shown to exert a similar effect and this conclusion is in marked contrast to the German assertion that the presence of phosphatides is the main cause of flavour reversion. Polyhydric alcohols such as sorbitol also increase the oxidative and flavour stability of the oils and it has been suggested that the effect of all these substances is to form inactive complexes with metal contaminants, particularly with iron derived from the deodorizing plant. The esters and salts of citric acid are not effective; neither is succinic acid.[31]

In a patented process, oils such as soya bean are subjected to thorough mixing with activated magnesium oxide which is claimed to remove the impurities causing the development of flavour reversion.[32]

Glyceride and fatty acid composition of various oils and fats

The fatty acid and glyceride composition of Bacury seed fat have been investigated and the unusually high proportion of trisaturated glycerides that had previously been reported has been confirmed. The fatty acid composition is given in Table I; the component glycerides were trisaturated 19·5% (including 14·5% tripalmitin), disaturated 55% (including 31% oleodipalmitin) and 25·5% monosaturated (including 16%

palmitodiolein). It is of interest to note that Bacury seed fat is an exception to the general rule that fully saturated glycerides do not occur to any appreciable extent in seed fats unless the proportion of unsaturated acids is less than is necessary to provide one molecule for each triglyceride molecule. Only two other exceptions have been noted as yet, namely, laurel kernel fat and the seed fat of *Myristica malabarica*.[33]

Dhupa fat or malabar tallow has been shown to contain 1% trisaturated, 73% disaturated (including 46% oleodistearin) and 23% monosaturated glycerides with 3% tri-unsaturated glycerides. The fatty acid composition is given in Table I, from which it is seen that stearic and oleic acids are the major components. The glyceride composition of Dhupa fat, like that of other Diptocarpaceae seed fats, is not marked by a preponderence of oleopalmitostearin as is the case with cocoa butter. All these fats contain approximately the same proportion of oleic acid but cocoa butter is much the most suitable as a confectionery fat. Its high content of oleopalmitostearin reduces its melting point and narrows the range of melting.[34] The glyceride constitution of corn oil has been computed from the analytical examination of 19 fractions obtained by crystallization of the oil from acetone. The results showed the presence of 56% tri-unsaturated, 40% di-unsaturated and less than 2% mono-unsaturated glycerides with 2% unsaponifiable matter. The main constituents were 48% oleodilinolein and 33½% monosaturated-dilinolein.[35]

The component glycerides of an Indian sheep body fat have been determined as fully saturated glycerides 28%, disaturated 28·5%, monosaturated 40·5% and tri-unsaturated 3%. The fatty acid composition of this fat is given in Table II. The glyceride composition differs from that of English sheep body fats in the higher proportion of fully saturated and monosaturated glycerides in relation to the total saturated acid content.[36] The fully saturated glyceride content of some New Zealand butterfats has also been reported to be slightly higher than would be expected from the saturated acids present.[37]

The glyceride structure of animal fats rich in stearic acid has been discussed with reference to the assertion that the high contents of trisaturated glycerides afford evidence in favour of a random distribution of the fatty acids between the glyceride molecules. It has been pointed out that this circumstance is fortuitous and that the di-unsaturated as well as the tri-unsaturated glyceride contents of these fats show a complete divergence from the values calculated from probability considerations. It is again suggested therefore that these fats are built up initially on an even distribution basis and that they are subsequently modified by processes of reduction in the animal body.[38] The content of fully saturated glycerides can be expressed as a ratio of the amount calculated from the saturated acid content on the assumption that random distribution occurs. This relationship has been suggested as a new characteristic value for fats. The figures for kernel fats of the Palmae ($1{\cdot}05 \pm 0{\cdot}02$) and for cow milk fats ($1{\cdot}12 \pm 0{\cdot}02$) are illustrative of the constancy of this ratio, which can vary from 2·02 for laurel kernel fat down to zero.[39]

An analysis has been made of the component acids of two specimens of common seal blubber (*Phoca vitulina*) and one sample of the liver oil. The results are given in Table II. The component acids of the liver

Table I

FATTY ACID COMPOSITION AND ANALYTICAL CONSTANTS OF SOME VEGETABLE OILS

		% oil	Density†	Refractive index†	Saponification value	Iodine value	Unsaponifiable matter	Palmitic	Stearic	Oleic	Linoleic	Linolenic
Abrus precatorius (Leguminosæ) ..	(42)*	2·5	0·9108 (24)	1·4702	187·5	90·6	1·3	1·1	4·6	46·0	12·6	18·5 (*a*)
Allium cepa (Indian onion) (Liliaceæ) ..	(43)	20·0	0·9364 (25)	1·4860 (25)	188·5	118·2	1·8	2·8	1·6	57·5	38·1	—
Beninkasa ceriferra (Whitegourd Melon) (Cucurbitaceæ)	(43)	36·4	0·9234 (30)	1·4740 (30)	194·5	135·3	1·3	8·5	4·0	19·2	68·3	—
Brassica alba (Yellow Mustard) (Indian)	(44)	39·5	—	—	172·6	102·2	3·8	1·5	0·4	22·0	14·2	6·8 (*b*)
Brassica nigra (Black Mustard) (Indian)	(44)	35·6	—	—	—	106·2	3·0	0·7	—	20·7	18·0	6·5 (*c*)
Calscarpum mammosum (Mexican) ..	(45)	—	0·9128 (25)	1·4690 (20)	188·4	73·5	1·83	← 36·8 →		37·5	23·8	—
Dodonea viscosa	(46)	18·6	0·9111 (30)	1·4734 (30)	196·7	110·9	0·82	13·1	16·5	23·9	29·8	— (*d*)
Elæis guineensis {Flesh	(47)	55–60	0·926–0·938 (15)	1·4486–1·4512	196–210	52–58	—	—	—	—	—	—
Elæis guineensis {Kernel	..	50·0	0·925–0·933 (15)	1·446–1·452	240–257	12–15	—	—	—	—	—	—
Euphorbia marginata	(48)	32·0	—	—	196·0	200·0	0·52	← 3·1 →		6·9	44·8	44·1
Gmelina asiatica (Badhara seeds) ..	(49)	7·5	0·9132	1·4645 (40)	191·7	100·4	2·2	9·4	19·3	32·9	25·2	— (*e*)
Hura polyandra (Mexican)	(45)	—	0·9188 (25)	1·4761 (20)	188·4	103·1	0·72	← 31·7 →		16·1	51·5	—
Jatropha curcas	(50)	44·0	0·9440 (29)	1·475 (27·5)	200·8	88·0	1·1	—	—	—	—	—
Lappa major (Great Burdock)	(51)	15·5	—	—	188·7	169·4	3·18	—	—	—	—	—
Lucerne leaf meal {glycerides	(52)	2·1	—	—	—	—	—	← 19·9 →		31·0	16·9	32·2
Lucerne leaf meal {phospholipids ..	..	0·24	—	—	—	—	—	← 13·3 →		36·8	14·7	35·2
Luffa ægyptiaca (Cucurbitaceæ) ..	(43)	40·0	0·9412 (27)	1·4830 (27)	194·9	106·4	1·2	9·6	7·3	40·5	42·6	—
Melilotus alba annus (Hubam clover) ..	(53)	7·6	0·9185 (25)	1·4741 (25)	180·1	141·0	5·9	← 1·5 →		—	—	—
Myrica cardifolia (Fruit-coat fat) ..	(54)	20·0	1·004 (15)	1·4504 (45)	214·7	0·6	0·12	51·8	0·3	0·6	—	— (*f*)
Ocimum graveoleus (Abyssinian basil weed)	(55)	18·6	0·942 (20)	1·4805 (20)	153·4	157·5	0·74	—	—	—	—	—
Oenocarpus batana (patana oil)	(56)	—	0·9158 (15)	1·4687 (20)	192·4	77·1	—	6·0	6·0	79·2	8·8	—
Okra seed	(57)	16·0	0·9170 (25)	1·4689 (25)	199·3	90·7	1·03	33·1	0·5	41·8	13·2 (?)	— (*g*)
Platonia insignis (Bacury seed) ..	(33)	—	—	—	—	40·4	0·78	55·1	6·4	31·7	2·3	— (*h*)
Rosafé wheat germ (Argentine) ..	(58)	—	—	1·4764 (20)	184·0	117·8	5·7	18·3	1·2	22·1	42·2	9·3 (*i*)
Sataria italica (Italian Millet) (Gramineæ)	(59)	6·0	0·9156 (25)	1·468 (25)	192·9	120·4	2·8	10·6	14·0	20·8	36·4	6·1 (*j*)
Sophora japonica	(60)	9·9	0·9238 (20)	1·4790 (20)	191·3	146·7	1·5	← 12·5 →		22·3	52·8	12·4
Swietenia macrophylla (Mexican) ..	(45)	—	0·9188 (25)	1·4726 (20)	196·1	104·0	1·39	← 25·7 →		24·5	48·4	—
Tangerine seed	(61)	—	0·9165 (25)	1·4702 (25)	193·5	107·3	0·54	—	—	—	—	—
Trichilia hirta (Mexican)	(45)	—	0·9277 (25)	1·4718 (20)	198·6	84·1	1·97	← 32·5 →		33·8	31·7	—
Vateria indica (Dhupa fat) (Dipterocarpaceæ)	(34)	—	—	—	189·9	41·5	1·1	9·7	40·7	42·2	2·3	0·5 (*k*)
Xanthium spinosum	(62)	7·9	0·920 (28)	1·4750 (20)	—	130·0	3·5	—	—	—	—	—
Zizyphus xylopyra (Rhamnaceæ) ..	(63)	—	0·9121 (26)	1·4725 (26·5)	192·8	84·4	0·8	—	—	47·3	24·6	— (*l*)

(*a*) Arachidic 5·1; Behenic 4·4; Lignoceric 2·5.
(*b*) Eicosenoic 7·0; Erucic 44·2
(*c*) Behenic 2·3; Lignoceric 1·8; Eicosenoic 8·1; Erucic 40·6
(*d*) Arachidic 5·4; Behenic 2·2; Erucic 7·2.
(*e*) Ricinoleic 11·0.
(*f*) Myristic 47.
(*g*) Myristic 3·8; Arachidic (?) 7·9.
(*h*) Hexadecenoic 3·2.
(*i*) Eicosenoic 3·7; Palmitoleic 2·1.
(*j*) Arachidic 6·3.
(*k*) Arachidic 4·6
(*l*) Myristic 28·1.

* The numbers in brackets in this column are those of the References at the end of the Chapter.
† The numbers in brackets in this column represent the temperatures (°C.) of determination.

Table II

FATTY ACID COMPOSITION AND ANALYTICAL CONSTANTS OF SOME ANIMAL AND MARINE OILS

	Indian sheep body fat[34]	Common seal (*Phoca vitulina*)[40]			New Zealand school shark (*Galeorhinus australis*)[41]					
		Blubber I	Blubber II	Liver II	Liver oils I	Liver oils II	Liver oils III	Liver oils IV	Head and body oil	Head and body phosphatides
Saturated acids										
Myristic	2·9	2·4	2·2	0·2	1·3	1·7	2·4	3·9	0·2	0·3
Palmitic	27·8	10·3	10·6	11·4	17·1	15·3	15·2	16·7	7·8	9·9
Stearic	27·7	2·5	4·4	7·8	6·5	3·4	3·6	5·3	19·0	13·3
Arachidic	1·5	0·3	0·3	0·1	1·5	1·1	—	0·1	5·2	0·3
Behenic	—	—	—	—	—	—	—	1·0	3·4	1·1
Unsaturated acids										
C_{14}	0·4 (−2·0)	2·9 (−2·0)	2·2 (−2·0)	—	0·6 (−2·0)	1·2 (−2·0)	1·1 (−2·0)	0·7 (−2·0)	0·2 (−2·0)	1·1 (−2·0)
C_{16}	2·7 (−2·0)	25·7 (−2·1)	20·8 (−2·1)	8·6 (−2·0)	5·4 (−2·0)	5·9 (−2·0)	6·2 (−2·0)	5·3 (−2·0)	5·2 (−2·0)	4·3 (−2·0)
C_{18}	(a) 33·0 (−2·0)	32·6 (−2·7)	33·7 (−2·4)	27·9 (−2·4)	25·4 (−2·6)	26·6 (−2·4)	31·7 (−2·4)	26·5 (−2·3)	13·5 (−2·2)	22·8 (−2·3)
C_{20}	0·6	12·1 (−5·9)	13·6 (−7·2)	23·7 (−6·2)	20·7 (−4·5)	19·5 (−5·8)	20·2 (−5·4)	15·5 (−4·5)	22·8 (−6·1)	16·1 (−6·5)
C_{22}		11·2 (−11·0)	12·2 (−11·0)	20·3 (−11·0)	21·5 (−7·6)	25·3 (−9·6)	19·6 (−8·8)	22·8 (−6·5)	22·7 (−12·0)	30·8 (−10·0)
C_{24}	—	—	—	—	—	—	—	2·2 (−4·0)	—	—
Unsaponifiable matter % ..	0·2	0·1	0·3	9·7	31·4	8·1	6·4	8·9	—	—
Saponification equivalent ..	284·8	289·0	292·0	—	410·0	317·1	319·6	321·0	—	—
Iodine value	39·4	140·0	145·4	—	185·0	178·0	170·7	149·0	—	—

(a) Plus 3·4 (−4·0)

glycerides are similar in composition to those of the blubber oil, whereas for the grey seal they are much less unsaturated. No phosphatides were found in the blubber oil from the common seal.[40]

The fatty acid compositions of a number of oils and fats are presented in Tables I and II. Minor amounts (less than 2·5%) of the constituent acids have been omitted when they cannot be conveniently included in these tables and the original papers should be consulted for further details. The temperature of determination is given in brackets after the figures for density and refractive index. In Table II, the degree of unsaturation is given in brackets after the percentage amounts of the fatty acids; for example (−2·0) signifies a mono-unsaturated acid.

Drying oils

It has been pointed out that the fall in the iodine number which occurs during the heat treatment of such oils as linseed oil is the net result of a number of reactions, some of which decrease the unsaturation while others increase it. Reactions also take place which have no effect on the iodine number. The elimination of a molecule of water from oxidized compounds at the higher temperatures can give rise to a new unsaturated linkage. This has been demonstrated by blowing rapeseed oil with air at 140° C., taking samples at intervals during the course of the reaction and then heating them at 200° C. without blowing. The samples increased rapidly in viscosity, and at the same time vigorous decomposition occurred with elimination of water. Definite increases in the iodine numbers were noted; in one instance, after 48 hours' heating the rise was from 52½ to 62. It was also shown that an increase in the iodine number can occur during the induction period. This was particularly marked when mixtures of rapeseed oil with 5 and 10% of linseed oil were air-blown at 110° C.: the viscosity remained unchanged.[64]

The oxidation and polymerization of linseed oil have been studied by determinations of the dielectric constant which was shown to increase from 3·2 to 5·1 during oxidation of the oil. The figure was practically constant at 5·1 over the viscosity range of 2200–3500 centipoises. The dielectric constant did not increase during thermal polymerization. Molecular weight determinations in *cyclo*hexane and the dielectric constant were recommended as valuable tools in plant control as well as in research.[65] A rapid molecular distillation method has been described for determining the degree of polymerization. Using small amounts of material, the method was reported to take only 20–30 min. The substance to be analysed was placed on a small plate suspended inside the distillation apparatus by a thin spiral glass spring. The material was heated by means of an infra-red lamp placed outside the apparatus and loss of weight during the distillation was indicated by contraction of the spring. Monomers evaporated first and then the dimers, the residue consisting of the higher polymers. Determinations were made on the polymerized esters of linseed oil fatty acids: analytical results obtained with known mixtures were good.[66]

Analysis of oils and fats

A paper on the problems associated with the analysis of synthetic fats and fatty acids has suggested an esterification test, similar to the

well known method for the determination of resin acids. Complete esterification of naturally occurring fatty acids is readily obtained in this test but the synthetic acids contain a fraction which cannot be esterified. The conclusion reached was that the unesterifiable acids contain a tertiary carboxyl group and that fats containing such acids are unsuitable for edible purposes.[67]

A new method has been described for the separation and estimation by partition chromatography of saturated fatty acids of intermediate chain length. Sulphuric acid (27–35N.) was used as the stationary phase and benzene as the mobile phase. Quantitative separation of formic, acetic, propionic, butyric, caproic, caprylic and capric acids was obtained; water was used as the stationary phase in some of the separations. The higher fatty acids did not interfere and they were determined separately as a group. Details of procedure were given for the quantitative analysis of the fatty acids from biological materials and an analysis of the fatty acids of butterfat was given, together with recovery results for known amounts of added acids. Ten micro-equivalents was the minimum amount of an acid that could be separated and determined.[68]

The average molecule weight of butterfat has been determined cryoscopically in benzene and found to vary from 660–682 for samples whose saponification values ranged from 221–236. The variation is less than that found for some of the more usual constants such as the Reichert and Polenske values and the iodine number and it was suggested that molecular weight determinations are of use for analytical purposes. Values of 824–833 were obtained for sesame oil and 602–610 for coconut oil: the molecular weights of mixtures were proved to be proportional to the known compositions. As would be expected, the presence of free fatty acids reduced the average molecular weight, but a correct value could be obtained when the fatty acids had been removed by washing with sodium hydroxide. Experiments were also made on butterfat that had been oxidized at 100° C. by bubbling oxygen through it. The molecular weight at first increased and then decreased to a value lower than that of the original fat.[69]

A series of papers has appeared on the chromatographic analysis of the unsaponifiable matter from vegetable oils. Chromatographic adsorption from benzene solution on aluminium oxide removes the sterols, the eluate containing the hydrocarbons. The iodine number of this hydrocarbon fraction indicates the squalene content and this is normally between 4 mg. and 36 mg.%. Olive oil contains 0·23–0·40% and brazil nut oil was shown to contain 0·15%. The difference between the total hydrocarbons and the squalene content is not usually more than 0·05% but grapeseed oil, wheat-germ oil and some olive oils were shown to have saturated hydrocarbon values greater than this. Values in excess of 0·05% were normally considered to indicate the presence of mineral oil and it was reported that as little as 0·1% could be demonstrated with certainty. In similar work on the unsaponifiable matter from teaseed oil, the substance responsible for the Fitelson test was isolated and named 'theasin.' It was adsorbed from benzene solution below the sterols on an aluminium oxide column. 0·2–0·3% was found in teaseed oil and a trace (0·03%) in olive oil. Analytical examination of theasin failed to

elucidate its exact nature but it was considered to be a diterpene derivative with the formula $C_{20}H_{34}O$.[70]

The tetrabromide method for the determination of linoleic acid in fatty acid mixtures has been exhaustively investigated. The method is empirical and the yields of tetrabromide are affected not only by the amount of linoleic acid but by the presence of the other fatty acids in the mixture. The composition of the light petroleum was shown to be important. Since the results were also considerably affected by the size of the sample taken for analysis, data were presented for 2 g., 1 g. and 0·5 g., samples showing the yields of tetrabromide obtained for known percentages of linoleic acid in admixture with oleic acid. These results were used in the preparation of three standard graphs, which could be used for the analysis of unknown mixtures. The limit of sensitivity of the method is 15–20% but within its obvious limitations the procedure is the best at present available. It is a specific reaction for linoleic acid and it was possible to prove the presence of this acid and to determine it in fractions obtained from the unsaturated acids of butterfat. The authors intend to repeat the work by determining the tetrabromide yields using a pure hydrocarbon such as *n*-pentane or *n*-hexane.[71]

A recently suggested method for the determination of linoleic acid in vegetable oils involves the oxidation of the fat with potassium permanganate in acetone and titration of the acidic glycerides after removal of the volatile acids of lower molecular weight. This method has now been stated to give high results, a figure of 58·5% having been obtained in one instance for a synthetic glyceride known to contain 40% of linoleic acid. The results of further experience with this method will be awaited with interest.[72]

British Standard Specifications have been published for tallow,[73] bone grease,[74] and tung oil.[75]

Soaps

There is little information available in the literature on the detergent properties of potassium silicates or on their use in soaps. It has been shown that a 40% potassium coconut oil soap is miscible in all proportions with a commercial silicate of 40% total solids ($K_2O : SiO_2$, 1 : 3·3). The foaming properties of the soap were considerably increased by admixture with the potassium silicate, the effect being much greater than that of potassium carbonate when the comparison was made on the basis of the alkali contents. The suspending power of the silicate solutions for ilmenite was almost as good as that of soap solutions but somewhat better than was obtained for a mixture of 80% soap with 20% silicate. However, with soap the maximum suspending power occurs at a higher concentration than for the silicate. The mixture was found to be practically as effective as the soap itself in preventing the deposition of ferric oxide on cotton cloth and slightly more effective in the case of raw umber. Detergency experiments showed the mixture to be about as efficient as soap when used in distilled water and more efficient in hard water.[76]

Considerable interest continues to be shown in aluminium soaps and their properties. A weak acid reacting with a weak base can hardly be

expected to produce a well-defined salt and when the numerous variables in the preparation of aluminium soaps are remembered it is not surprising that results are difficult to duplicate. Until they have been dried, aluminium soaps prepared from aqueous solutions have a negligible solubility in hydrocarbons at ordinary temperatures. Experiments have been reported in which aluminium soap has been formed by the interaction of aluminium alcoholate and fatty acid. In the absence of water, the product was very soluble in benzene and the solution did not gel. The addition of water caused marked gelling and rise in viscosity, which increased to a sharp maximum when one molecule of water per molecule of soap had been added. The position of this maximum was independent of the relative or the total amount of fatty acid reacted, but the highest maximum was obtained for two molecules of fatty acid per molecule of aluminium alcoholate. The results confirm the conclusion reached by many investigators that the aluminium tri-soap does not exist.[77] Work on the reaction between fatty acids and aluminium *sec.*-butoxide showed that three molecules of alcohol can be distilled from the product for every molecule of aluminium alkoxide reacted, but determinations of the heat of reaction and analysis of the products showed that the soaps contained no more than 1½–2 molecules of fatty acid. Reaction of the alkoxide with water was completed when two molecules had reacted. Even when the amount of fatty acid reacted was decidedly less than one equivalent, the resulting products contained more than 1 molecule of fatty acid per molecule of soap. It was concluded that the tri-soap and the mono-soap do not exist.[78]

An examination of aluminium stearate precipitated from aqueous solution has shown that the excess fatty acid is present in two different forms which can be distinguished by their solubility in solvents such as acetone. The free stearic acid is readily dissolved up to the limit of its normal solubility, but loosely bound or adsorbed acid is also present which is not completely removed even when the solvent is by no means saturated with stearic acid. The chemically bound acid which cannot be extracted corresponds to the formula for the distearate.[79]

Detergency

The surface tension of dilute aqueous solutions of soaps and synthetic detergents passes through a minimum as the concentration is increased. On the other hand, the adsorption of surface-active agents is always positive and this apparent contradiction is explained in the case of soap by the probability that acid soap formed by hydrolysis is strongly concentrated in the surface layer. Such a hypothesis is not however possible for substances that are not readily hydrolysed, such as the alkyl sulphates and the alkyl sulphonates. It was shown some years ago for sodium alkyl sulphates that the pure substance does not give this minimum in the surface tension curve and that the presence of small amounts of surface-active impurities is responsible for this phenomenon. These apparently become solubilized by colloidal micelles at the higher concentrations of the detergent and are in this way removed from the sphere of action. It has now been demonstrated that the minimum surface tension effect is not obtained with purified lauryl sulphonate and that

lauryl alcohol present as impurity has quite a marked effect at a concentration as low as 0·05%. The impurities causing the minima may be eliminated by foam fractionation of solutions of lauryl sulphonate and of sodium lauryl sulphate at concentrations just below the critical concentration for micelles, that is, near the point where the surface tension is at a minimum. It was found that the minimum was much more pronounced in the foam fraction and that it disappeared entirely from the foam extracted material. Similar results were obtained by emulsion extraction. A characteristic of the impure solutions is that the surface tension falls slowly over long periods of time; it was noted that this ageing effect was much less marked for the purified solutions. A large decrease in foam stability was qualitatively evident when the detergents were purified.[80,81]

The importance has been demonstrated of the penetration by detergent solutions into the internal capillary regions of individual fibres as distinct from penetration between the yarns of a fabric and between the fibres themselves. Observations under the microscope showed that adherent drops of oil increased in size as air was displaced by the detergent from the internal regions of the fibre. In many cases the buoyancy of the drops was increased to such an extent that they could be shaken off by the slightest agitation.[82]

Several papers have appeared in which the detergent process has been considered as analogous to a reversible chemical reaction with a position of equilibrium affected by the factors that normally influence detergency.[83] When cotton fabric was shaken with a suspension of carbon in a detergent solution, a narrow critical range of concentration was found below which the fabric was badly soiled and above which the whiteness of the material was well retained. This critical concentration was shown to be dependent on the amount of dirt, the graphical relation between the two being a straight line passing through the origin. This was interpreted as an indication that micelle formation is not an important factor in the process. The slope of the curve was different for different detergents. The relation between whiteness retention and the detergent concentration was also shown to vary for different detergents. The results were discussed on the basis of an equilibrium in the following reversible reaction—soap + dirt $\rightleftharpoons$ soap : dirt.[84] The conclusion that suspending power was not due to solubilization by the colloidal properties of the solution was also reached in an investigation into the suspending power of detergent solutions for manganese dioxide. Suspension was considered to be the result of a deflocculating effect on aggregated particles due to adsorption of simple ions from solution. Maximum suspending power was shown at low concentrations of the detergents: a non-ionic detergent was found to possess no suspending power in spite of its high surface activity and the presence of colloidal micelles.[85]

In connexion with such work, however, we have been reminded that the nature of the surface to be cleaned cannot be disregarded and that a substance having a high suspending power is not necessarily a good detergent. A simplified method has been described for measuring the dispersing power of detergents for oiled umber. Among the detergents tested by this method sodium lauryl sulphate and alkyl-aryl sulphonates

gave fairly good results and non-ionic detergents were somewhat better: soaps were found to have very high dispersing powers.[86]

Of the variable factors influencing detergent operations the one which has received least attention is undoubtedly mechanical work. A certain amount of cleansing action is of course obtainable by mechanical work with water alone. The effect of a detergent is to reduce the forces holding the dirt to the fabric and less work is then required to remove it. It has been suggested therefore that a comparison of detergents can be made at equal concentrations by measurement of the mechanical work required to effect equal removal of soil. The experiments were carried out in a launderometer, the mechanical work being varied by using different numbers of different sized balls and by running the machine at two different speeds. In this way a 'force scale' was arbitrarily evaluated in 24 units. Soiled fabric was washed at 120° F., and the amount of dirt removed was computed from reflectance values. These results were corrected for the effect obtained by prerinsing the fabric with water alone. The variables studied were detergent concentration, time and mechanical force. For a given degree of soil removal, concentration of detergent was inversely proportional to the force required and also to the time. It follows, therefore, that the time and the mechanical force were also inversely proportional, and the results were found to conform to the equation $S = K\ (CTF)^n$, where K and n are constants, C is the detergent concentration, T is the time and F is the mechanical force expressed in arbitrary units. These relationships were not valid in the range of very low soil-removal, or above the point at which increase in concentration of detergent fails to cause increased soil removal.[87]

The necessity for using an oil-based soil in detergency work has recently been questioned. Cotton cloth was soiled to the same extent both with and without a binding agent. No difference in the ease of soil removal was found to result from the presence of a binding agent either of an oily or a water-soluble type.[88]

The evaluation of ternary mixtures of synthetic detergent with soap and builders has been made by the determination of p_H, foaming power and detergent power (using soiled cotton). Trisodium phosphate and tetrasodium pyrophosphate both showed a 'synergistic' effect with soap and with synthetic detergent, the effect being quite marked with tetrasodium pyrophosphate. Ternary mixtures of soap, synthetic detergent and tetrasodium pyrophosphate were examined and, of the two mixtures with highest detergent power, one had a low and the other a high foaming power. These mixtures were both better, at 0·4% concentration, than either the soap or the detergent. The soap used was sodium stearate; the detergent was an alkyl-aryl sulphonate containing 40% active ingredient and 60% sodium sulphate.[89] It has been reported that the detergent power of an alkyl-aryl sulphonate was increased by the addition of a non-ionic detergent and that the improvement was obtained also when sodium carboxymethyl cellulose was present. The replacement of half the soap in a detergent formula by non-ionic detergent improved the detergent power in hard water. The formula contained carboxymethyl cellulose, sodium carbonate and tetrasodium pyrophosphate in addition to the soap.[90]

In a recent investigation on the desoiling properties of carboxymethyl cellulose, its ability to reduce redeposition of soil was again demonstrated. Although it was also proved that carboxymethyl cellulose had no detergent or soil-removing properties there was some evidence, obtained in experiments with a factorial design, that it did enhance the desoiling properties of the non-ionic detergent used in the tests.[91]

A preliminary report has been made on the detergent effect obtained by the use of supersonic vibrations. Although there was no visible agitation of the washed material, the detergent effect was satisfactory and there were no strength losses.[92]

Further work on the action of diphase metal cleaners containing mineral spirits, water and triethanolamine oleate has shown that such cleaners are much more effective when the solvent is not substantially emulsified in the aqueous phase. A good emulsion has practically no effect in removing an oil-based soil since one of the advantages of such cleaners is the simultaneous action of an aqueous and a solvent phase. These conclusions were confirmed in tests on the cleaning of steel sheets soiled with grease and dust, as well as with the contamination resulting from their manufacture.[93]

Attention is drawn to several reviews on the subject of detergents and detergency.[94,95,96]

Analysis of soaps and detergents

Conductimetric methods of determination have been shown to give satisfactory results for fatty and resin acids and for excess of these acids when present in soaps. Indirect titrations with alkali after the addition of a known amount of acid enabled the soap content and the free fatty acid content to be determined in a single titration. Satisfactory results were obtained for the direct titration of the combined alkali in soaps, and free alkali if present could also be determined. Potentiometric titrations were, however, only satisfactory for the determination of fatty and resin acids. The resin soaps could not be titrated and the results for fatty acid soaps were less satisfactory than the conductimetric determinations. The titrations were made in 50% solutions of *iso*propyl alcohol.[97]

Pinacyanol bromide (0·001N-solution) has been suggested as an indicator for the titration of anionic with cationic detergents[98] and a new method for the determination of non-ionic detergents has been described. Hydrochloric acid, barium chloride and phosphotungstic acid are added to a solution containing not more than 100 mg. of the detergent and a yellowish green precipitate is obtained. In the example given, the weight of the precipitate was almost exactly three times that of the sample taken, but the ratio is dependent on the nature of the detergent.[99]

In a new method of evaluating detergents the use of fibres has been suggested instead of the conventional textile piece. The fibres were soiled uniformly with a mixture of graphite and liquid paraffin. They were then suspended in a solution of the detergent and stirred by means of a plunger moving up and down at 70 strokes per minute. At the end of the operation the fibres were filtered off and the wad or pad of washed fibres was fixed by means of a solution of polyvinyl alcohol. The colour

of the pad was measured in a reflectance photometer with light at 45° incidence. Results were reproduced with an accuracy of ±5%, an accuracy which can only be obtained with fabric by the use of numerous test pieces. The advantages of this method will be readily apparent: variations in the degree of soiling are averaged out and photometric measurements are more easily made. Because of the uniform texture of the wad only one reading need be taken, whereas at least eight measurements are usually made on a washed test-piece.[100]

The evaluation of detergent efficiency by laboratory reproduction of continuous factory operations has been described. For example, in the scouring of raw wool the quality of the washed product will deteriorate slowly until a point is reached when a new addition of detergent is required. In such a case, the efficiency of the detergent will not be measured by its initial performance (provided of course that this is satisfactory) but by its ability to maintain a certain minimum quality in the finished product. By reproducing the factory process in the laboratory it was possible to determine the optimum conditions by investigating the effect of variation of such factors as immersion time, squeeze pressure, temperature, concentration and type of detergent.[101]

A comparison has been made of a number of methods for measuring the wetting time of textiles by the detergent solution. It was found that the various detergents were not necessarily placed in the same order by the different methods or even by modifications of the same method. It was apparent, however, that for any particular test, the logarithm of the wetting time varied directly with the logarithm of the concentration. The slope of this curve was shown to be a characteristic of the wetting agent and to be the same whatever the exact nature of the test. It was emphasized that the comparison of detergents and wetting agents should not be made by means of a single measurement of the wetting time unless it is known that the slopes of the wetting curves are similar. If the slopes are different it is apparent that one detergent increases its wetting power faster than the other as the concentration is increased.[102]

A British Standard Specification has been published for liquid toilet soap.[103]

References

1 Karon, M. L. and Hillery, B. E., *J. Amer. Oil Chem. Soc.*, 1949, **26**, 16
2 Williams, P. A. *et al.*, ibid., 28
3 King, R. R. and Wharton, F. W., ibid., 201
4 Idem, ibid., 389
5 Passino, H. J., *Ind. Eng. Chem.*, 1949, **41**, 280
6 Bailey, A. E., *J. Amer. Oil Chem. Soc.*, 1949, **26**, 166
7 Bataille, R., *Oléagineux*, 1948, **3**, 532
8 Callery, E. L. d'A., B.P. 621,037
9 Paquot, C. and Richet, R., *Oléagineux*, 1948, **3**, 26
10 Lever Bros. and Unilever Ltd., B.P. 611,508
11 Akties. Grindstedvaerket, B.P. 614,925
12 Feuge, R. O. and Gros, A. T., *J. Amer. Oil Chem. Soc.*, 1949, **26**, 97
13 Naudet, M., Micaelli, O. and Desnuelle, P., *Oléagineux*, 1948, **3**, 57
14 Reutenauer, G. and Sisley, J. P., ibid., 305
15 Eckey, E. W. and Formo, M. W., *J. Amer. Oil Chem. Soc.*, 1949, **26**, 207
16 Ittner, H. H. (to Colgate-Palmolive-Peet Co.), U.S.P. 2,474,740
17 Ross, J., Gebhart, A. I. and Gerecht, J. F., *J. Amer. chem. Soc.*, 1949, **71**, 282

[18] Allen, R. R., Jackson, A. and Kummerow, F. A., *J. Amer. Oil. Chem. Soc.*, 1949, **26**, 395
[19] Lundberg, W. O., Chipault, J. R. and Hendrickson, M. J., ibid., 109
[20] Lewis, W. R. and Quackenbush, F. W., ibid., 53; Lewis, W. R., Quackenbush, F. W. and De Vries, T., *Analyt. Chem.*, 1949, **21**, 762
[21] Achaya, K. T., *Biochem. J.*, 1949, **44**, 561
[22] Paul, T. M. *et al.*, *Indian J. vet. Sci.*, 1947, **17**, 95
[23] Iselin, E., *Mitt. Lebensmitt. Untersuch. Hyg.*, 1948, **39**, 310
[24] Idem, ibid., 1949, **40**, 105
[25] Swift, C. E. *et al.*, *J. Amer. Oil Chem. Soc.*, 1949, **26**, 475
[26] Kraybill, H. R., *et al.*, ibid., 449
[27] Dassow, J. A. and Stansby, M. E., ibid., 475
[28] Stevens, H. H. and Thompson, J. B., ibid., 1948, **25**, 389
[29] Jarowski, C. I., U.S.P. 2,455,256
[30] Taylor, W. G., *J. Amer. Oil Chem. Soc.*, 1949, **26**, 413
[31] Dutton, H. J., *et al.*, ibid., 1948, **25**, 385; ibid., 1949, **26**, 441
[32] Moyer, W. W. and Marmor, R. A., U.S.P. 2,454,937
[33] Hilditch, T. P. and Pathak, S. P., *J. chem. Soc.*, 1949 (Suppl. issue) S.87
[34] Baliga, M. N. and Meara, M. L., *J. Soc. chem. Ind.*, 1949, **68**, 52
[35] Doerschuk, A. P. and Daubert, B. F., *J. Amer. Oil Chem. Soc.*, 1948, **25**, 425
[36] Hilditch, T. P. and Shrivastava, R. K., ibid., 1949, **26**, 1
[37] Ting, I., *N.Z. J. Sci. Tech.*, 1948, **29**, 240
[38] Hilditch, T. P., *J. Amer. Oil Chem. Soc.*, 1949, **26**, 41
[39] Sukumaran Kartha, A. R. and Menon, K. N., *Proc. Indian Acad. Sci.*, 1948, **27**, 279
[40] Hilditch, T. P. and Pathak, S. P., *Biochem. J.*, 1949, **44**, 218
[41] Oliver, A. P. and Shorland, F. B., ibid., 1948, **43**, 18
[42] Mandiratta, M. J. and Dutt, S., *Indian Soap J.*, 1948, **14**, 195
[43] Phadnis, K. D., *et al.*, *J. Univ. Bombay*, 1948, **17** (3), 62
[44] Kapur, S. L. and Daubert, B. F., *J. Amer. Oil Chem. Soc.*, 1949, **26**, 472
[45] Munguia, R. R., *et al.*, ibid., 431
[46] Kochar, R. K. and Dutt, S., *Indian Soap J.*, 1948, **14**, 132
[47] Pujol, M. P., *Rev. ind. y fabril.*, 1948, **3**, 572
[48] Albertsma, N. A., *Paint Manuf.*, 1949, **19**, 135
[49] Aggarwal, J. S. and Soni, P., *J. sci. industr. Res., India*, 1949, **8B**, 49
[50] Desai, C. M. and Vyas, M. T., *Curr. Sci.*, 1949, **18**, 49
[51] Kunert, G., *Pharm. Ztg., Berlin*, 1948, **84**, 332
[52] Jackson, A. H. and Kummerow, F. A., *J. Amer. Oil Chem. Soc.*, 1949, **26**, 26
[53] Clopton, J. R. and Roberts, A., ibid., 11
[54] Schoeman, D. J. and Hawke, P., *J.S. Afr. chem. Inst.*, 1948, **1**, 5
[55] Valyashko, N. A. and Nepomnyaschaya, Z. A., *Zh. Prikl. Khim.*, 1947, **20**, 151
[56] Chaves, J. M. and Pechnik, E., *Quim. e industr.*, 1946, **14**, No. 112 (147), 2
[57] Clopton, J. R., Roberts, A. and Jeskey, H. A., *J. Amer. Oil Chem. Soc.*, 1948, **25**, 401
[58] Guitarte de Fortunato, E. J., *Industr. y Quím.*, 1948, **10**, 127
[59] Pargal, H. K. and Dutt, S., *Indian Soap J.*, 1948, **14**, 81
[60] Cornea, I. and Rudenco, A., *Bul. Inst. Nat. Cerc. Tech.*, 1948, **3**, 48
[61] Swift, L. J., *J. Amer. Oil Chem. Soc.*, 1949, **26**, 438
[62] Carr, C. J., *J. Amer. pharm. Ass.*, 1949, **38**, 243
[63] Airan, J. W., *Curr. Sci.*, 1948, **17**, 150
[64] Gillam, N. W., *J. Aust. chem. Inst.*, 1948, **15**, 126
[65] O'Hare, G. A., Hess, P. S. and Kopacki, A. F., *J. Amer. Oil Chem. Soc.*, 1949, **26**, 484
[66] Booy, H. and Waterman, H. I., *Analyt. chim. Acta*, 1949, **3**, 440
[67] Sandermann, W., Casten, R. and Scharnberg, W., *Pharmazie*, 1948, **3**, 211
[68] Peterson, M. H. and Johnson, M. J., *J. biol. Chem.*, 1948, **174**, 775
[69] Phatak, S. S., Dole, K. K. and Karve, D. D., *J. Univ. Bombay*, 1948, **17** (3), 29
[70] Hadorn, H. and Jungkunz, R., *Mitt. Lebensmitt.-Untersuch. Hyg.*, 1948, **39**, 259; 1949, **40**, 61 and 96
[71] White, M. F. and Brown, J. B., *J. Amer. Oil Chem. Soc.*, 1949, **26**, 385
[72] Kartha, A. R. S., Menon, K. N. and Raman, P. S., *Curr. Sci.*, 1949, **18**, 8
[73] B.S. 1482 : 1948

[74] B.S. 1483 : 1948
[75] B.S. 391 : 1949
[76] Merrill, R. C. and Getty, Y., *J. Amer. Oil Chem. Soc.*, 1949, **26**, 5
[77] McRoberts, T. S. and Schulman, J. H., *Nature*, 1948, **162**, 101
[78] Gray, V. R. and Alexander, A. E., *J. phys. colloid Chem.*, 1949, **53**, 23
[79] Coe, R. H., Mysels, K. J. and Smith, G. H., *J. Colloid Sci.*, 1948, **3**, 293
[80] Brady, A. P., *J. phys. colloid Chem.*, 1949, **53**, 56
[81] Shedlovsky, L., Ross, J. and Jakob, C. W., *J. Colloid Sci.*, 1949, **4**, 25
[82] Powney, J., *J. Text. Inst. Manchr.*, 1949, **40**, 519T
[83] Schwartz, A. M., *J. Amer. Oil Chem. Soc.*, 1949, **26**, 212
[84] Gruntfest, I. J. and Young, E. M., ibid., 236
[85] Greiner, L. and Vold, R. D., *J. phys. colloid Chem.*, 1949, **53**, 67
[86] Snell, F. D. and Reich, I., *J. Soc. chem. Ind.*, 1949, **68**, 98
[87] Bacon, O. C. and Smith, J. E., *Ind. Eng. Chem.*, 1948, **40**, 2361
[88] Utermohlen, W. P. *et al.*, *Text. Res. J.*, 1949, **19**, 489
[89] Morrisroe, J. J. and Newhall, R. G., *Ind. Eng. Chem.*, 1949, **41**, 423
[90] Barker, G. E., *J. Amer. Oil Chem. Soc.*, 1949, **26**, 304
[91] Feuell, A. J., *J. Text. Inst. Manchr.*, 1949, **40**, 523T
[92] Schilling, H. K. *et al.*, *J. acoust. Soc. Amer.*, 1949, **21**, 39
[93] Reich, I. and Snell, F. D., *Ind. Eng. Chem.*, 1948, **40**, 2333
[94] Anon., *Mfg Chem.*, 1949, **20**, 442
[95] Snell, F. D., *Chem. & Ind.*, 1949, 539
[96] Paice, E. S., *J. Text. Inst. Manchr.*, 1949, **40**, 876
[97] Maron, S. H., Ulevitch, I. N. and Elder, M. E., *Analyt. Chem.*, 1949, **21**, 691
[98] Salton, M. R. J. and Alexander, A. E., *Research*, 1949, **2**, 247
[99] Oliver, J. and Preston, C., *Nature*, 1949, **164**, 242 . .
[100] Powney, J. and Feuell, A. J., *Research*, 1949, **2**, 331
[101] Leonard, E. A. and Winch, A. R., *Rayon Synth. Text.*, 1949, **30** (1), 79 and (2), 93
[102] Edelstein, S. M. and Draves, C. Z., *Amer. Dyest. Rep.*, 1949, **38**, 343
[103] B.S. 1545 : 1949

COSMETICS AND TOILET PREPARATIONS

By R. H. MARRIOTT, D.Sc., F.R.I.C.

THE literature covering the science of cosmeticology extends from the chemistry of dyes and colouring matters, fats, oils and waxes and derivates thereof, to the physics and physical chemistry of combinations of the multitudinous substances used, to say nothing of the biology of the living tissues. Especially is it important that the cosmeticologist should know something about allergy since whatever is vended to the consumer must be 'safe'; any preparation which is liable or prone to cause a dermatitis quickly ceases to be a profitable production. Partly owing to this wide coverage and partly because it is only recently that trained, scientifically-minded executives have entered the industry, there is hardly yet a coherent, collected background of knowledge which can be called Cosmetic Science and Technology.

The industry suffers much from its empiricism which leads to an intensely guarded secret 'know-how,' with the inevitable result that such writings as are found in the technical press tend to be diffuse as to principles but profuse as to formulae. One has only to turn over the pages of the publications to observe the almost unlimited number of recipes and then to note how lacking is the explanation of why this or that is included and why this percentage or that percentage is used. It is to be noted, however, that during the last decade reports of the older type are being supplanted by more precise and reasoned papers. This progress is not unique: it has occurred in all the old industries during the last 50 years. That it should have happened so late with the cosmetic industry is probably due to its later expansion into one of notable size. It is difficult to give up-to-date figures but according to the recently published figures issued by the U.S. Bureau of the Census, the value of perfumes, cosmetics and toilets sold in the States in 1947 amounted to no less than 425 million dollars.

Somewhat naturally, much of the chemist's attention has been given to devising suitable tests for both the raw materials and the finished products. Much of the work in this connexion has been collated and published with the aid of the Toilet Goods Association of America (T.G.A.), standard methods of carrying out the tests having been described. At the later part of 1948 and during 1949, Navarre[1] has published a very comprehensive and detailed list of materials and the methods of analysis. These methods are shortly to be published in book form and they should be a welcome addition to the cosmeticologist's library. T.G.A. specifications have been issued for certain materials which are of importance, notably petroleum hydrocarbons, mineral oil,[2] petroleum jelly,[3] paraffin wax (crystalline),[4] paraffin wax (microcrystalline),[5] methyl cellulose (i.e. methyl ether of cellulose),[6] and ammonium thioglycollate.[7] As regards other common materials, attention should be drawn to the two reports of the Sub-Committee of the Society of Public Analysts,[8] who have drawn up methods by which a reasonable estimate of the quality of gum

tragacanth can be made. Specifications and analytical methods for precipitated chalk, magnesium carbonate, propylene glycol and anhydrous lanolin have been given.[9]

Little published work relates, however, to the analysis of the finished products. Atkins[10] draws attention to the desirability of knowing the individual substances which may be present. For example, in a face powder it is necessary to know what anion is combined with which cation, and he has devised a suitable scheme of analysis. The identification of coal tar colours has been dealt with by K. A. Freeman[11] while P. Velon[12] has discussed the various chemical and physical methods by which quality can be determined. This paper is important as it covers methods of measuring density, viscosity, etc., and includes an excellent bibliography. He appears to favour the modified Brinell apparatus of E. Mahler[13] who employs a right-angled cone instead of the usual ball for measuring body or consistency. Marriott[14] has described the use of a rotating-cup viscometer for the evaluation of cosmetical and pharmaceutical creams and pastes. The problem of differentiating animal and vegetable oils has been investigated by M. Staub,[15] who claims that the peroxidation of most animal oils can often be distinguished and detected by means of titanous sulphate.

A general review of cosmetical and toilet preparations was given by Marriott[16] in which the commoner creams and lotions were described and the basic principles of how they act when applied to the skin and hair. It was indicated that in the case of face powder the actual criterion was not entirely one of fineness of particle, but that the opacity was of considerable importance. Nevertheless, Hinkel, Nachod and Trainter[17] have investigated the average particle size of various types of cosmetic powder by means of the air permeability method of Gooden and Smith[18] and find that proprietary talcum powders have a larger particle size than baby powder, while face powder is still finer.

Powdering the face is mostly done by loose powder and a puff, but the newer forms are notably of the cake type. Kempson-Jones[19] has given a short account of them and also of the newer liquefying make-up creams. He has also described the manufacturing technique and has given formulae for rouge compact.[20] E. S. Lower[21] has described cream rouge and lipstick, advocating the use of tetrahydrofurfuryl alcohol and its esters as a solvent for eosin and as a plasticizer.

Immediately after the war, there was a distinct trend towards making cosmetical creams of a protective character, the inspiration being obtained from the war-time experience of barrier creams in the factories, insect repellents and sun-screening agents for the armed forces. It is early yet to say how the household use of barrier creams will develop, but although the insect-repellent preparations functioned well with the armed forces, there does not seem to be much future for them with the public. McAllister[22] has reviewed and described a number of these substances and shows how their 'life' depends on the amount of perspiration. It is probable that some newer mode of presentation will have to be devised. Happhe and Sodergreen[23] have obtained a patent covering the intimate mixing of the repellent and also sun-screening agents in clay, kieselguhr, aluminium hydroxide, etc., which is then dispersed in a cream.

Treatment of hair; permanent-waving preparations

Little attention has been given to hair preparations such as brilliantines, cream, etc. The major activity has been centred around permanent-waving preparations, especially of the 'cold' variety. These preparations were first introduced to the American market in 1943 and their sales have been enormous. They entered the British market at the beginning of 1948 and have shown a similar, though perhaps not so spectacular rise, here. Since the dominant agent used is ammonium thioglycollate, which has a vigorous action on keratin, it is obviously of the first importance that a clear picture must be available of how the waving agent functions. Reed, Debente and Humoller[24] have given an extensive account of the chemical reactions involved; Speakman,[25] who probably was the original inventor in this field, has explained the result as being due to two consecutive reactions: the breakdown of cystine linkages and the rebuilding of new linkages which restore strength to the hair and give permanence to the wave. He draws attention to the dangers attending the use of reducing agents. These warnings are probably based on Speakman's experience of the damage sustained by reduced wool even when cross-linking is brought about after the reduction.[26] The effect of the cold-waving materials on the general health of the subject has been investigated by the American Medical Association[27] who report not unfavourably about them. On the other hand, the direct sale of outfits containing thioglycollic acid or its salts to the public has been forbidden in France.[28] The desire to obviate the chance of untoward effects and also to give greater convenience in handling these reagents has led to 'improved' forms, e.g. emulsified products such as is described by Mace.[29]

For an account of the more academic work on the chemistry of hair, reference should be made to the chapter on Cellulose Textile Chemistry. Attention is drawn to the work of Farnworth, Neish, and Speakman[30] who have verified the part played by break-down of the disulphide links in chemical anti-shrink treatments by converting the disulphide into a thio-ether link by means of 0·1M–KCN at 66° C. Agents such as Cl_2, SO_2Cl_2 and NaOH failed to make such wool unshrinkable. Blackburn and Lindley[31] have investigated set and super-contraction in wool in which the carboxyl group has been methylated. This leads to reduction of the force between the side chains and increases the positive charge of the fibre. The reduction in internal stress should reduce the super-contraction and also the force opposing set, an hypothesis supported by their results. Although some of the findings are unexplained, the significance of the hydrogen bond is stressed. The possibility that super-contraction is caused by two distinct mechanisms is indicated by Alexander,[32] who has shown that wool treated with alkali no longer contracts in boiling aqueous bisulphite but does so in concentrated lithium bromide solution.

The possibility does exist of bringing about a more or less permanent wave in hair or wool by infiltration with polymers and much work has been done on this by Speakman and his school. Lipson and Speakman[33] have polymerized vinyl derivatives inside wool fibre using ferrous ammonium sulphate and hydrogen peroxide as initiators. Reduced

wool appears to provide its own catalyst and methacrylic acid will readily polymerize in wool which has been treated with thiolacetic acid (Lipson[34]).

The notion of fixing hair in a wave by coating it with a transparent rigid material is an old one, mucilages made from gums and similar hydrophilic colloids being the popular choice. Notably during the last year, new materials have been put forward and found a ready market. Unfortunately, many of them have experienced a rapid decline owing, probably, to the use of wrong materials. One of the newer forms, which is vended in tiny capsules, the contents of which have to be dissolved in water, contained ferrous–ferric iron mixed with citric acid[35]; it has been condemned by the hairdressing profession on the grounds that hair so treated was readily damaged if it were subsequently bleached, whereas the hair became discoloured if it were waved.[36] It has been suggested that such hair is liable to become pink when treated with thioglycollate.

The dyeing of hair has advanced but little during recent times; the *para* dyes, in spite of their shortcomings, still remain dominant in this field. R. L. Evans[37] has reviewed the position and has suggested that the *p*-phenylenediamine technique is dependent on the use of material of small molecular size and the ability to condense, on oxidation, to coloured bodies which are fast to light and washing; the shades produced can easily be modified by the use of metallic mordants. Non-toxic dyes are claimed to have been produced by the Laboratoire Garnier[38] but their composition has not yet been divulged.

Interest in the natural pigment, melanin, has been shown by the publication of two papers by H. S. Mason and J. Harley Mason[39] at the First International Congress of Biochemistry.

Depilatories of the modern type have been reviewed by Van Sluis[40] who deals mainly with the organic sulphides and cites patents covering the use of the various active depilating agents, e.g. thioglycerol.[41] The removal of hair by the more usual method, i.e. by shaving, demands some preparation which can soften the hair and act as a lubricant for the razor. Winter[42] has given formulae for shaving soap creams and the use of salt solutions for controlling their consistency.

The problem of washing hair has attracted much attention. The search for newer and better shampooing agents still goes on. R. Leslie[43] has reviewed the American field of anionic, cationic and non-ionic detergents and gives a list of the more important ones. Oil shampoos are discussed and formulae are given,[44] and powder and liquid shampoos have been reviewed.[45] On the general theory of detergency and especially with regard to hair, reference should be made to the chapters on The Protein Fibres and on Fats, Fatty Oils and Detergents.

Toothpastes

The cleaning of teeth is probably all that can be claimed for a dental preparation. New toothpastes in which ammonium phosphate and urea are incorporated have been put on the market, but how far these preparations can be claimed to reduce or control the incidence of dental caries has yet to be proved. A. G. Arend[46] has described the modern methods of compounding toothpastes in order to ensure stability and

consistency. The evaluation of dental creams has been investigated by Phillips and Van Huysen[47] by noting the loss in weight of teeth when treated with fruit juices, e.g. orange and lemon. They find that although the p_H value is the dominant factor its effect can be modified by increase of the calcium and phosphate content. They have also examined the effect of various powders on the lustre and find that of the common ingredients of toothpastes, sodium metaphosphate plus calcium phosphate give a positive polishing whereas calcium carbonate reduces the lustre. It should, perhaps, be pointed out that all their experiments were done on dead teeth.

It is well to realize that the vast majority of toilet and cosmetical products are multi-phase; as oils, fats and waxes are extensively used, the cosmetic chemist must have some considerable knowledge of emulsions; an *ad hoc* experience is often of great value, especially as much of the academic work is carried out with pure substances rather than the commercial ones. A. M. G. Rutton[48] gives a number of formulations for the preparation of O/W and W/O emulsions using ethanol- and propanolamine soaps. Notable newcomers in this field are the polymerized ethylene glycol monostearates.[49] A series of these substances is available, the solubility of which decreases in non-polar solvents with increasing amount of ethylene oxide. Concomitantly the solubility in water increases, giving increasing wetting and penetrating properties. By suitable choice almost all types of emulsions can be made with almost any ingredients. The advantages of these substances is that they are odourless and are not affected by electrolytes such as aluminium sulphate, etc.

J. Pickthall has given an excellent lecture on emulsification and emulsions[50] to the Society of Cosmetic Chemists of Great Britain; the full lecture has unfortunately not yet appeared in print.

It is to be appreciated that much of the works' scientific staffs' time is occupied in control of the quality and the suitability of packaging materials. In this review no reference has been made to this important aspect of the industry. The reason for this is that the problems involved are so diverse that the subject might easily take up the major part of this Report. At any rate, the cosmetic chemist will be well advised to scan those other Reports which deal with substances of which the packages are made.

References

1 *Soap, Perfum. Cosmetics*, 1949, **22**, Nos. 1–8
2 Ibid., 278
3 Ibid., 279
4 Ibid., 281
5 Ibid., 282
6 *Perfum. essent. Oil Rec.*, 1949, **40**, 166
7 Ibid., 167
8 *Analyst*, 1948, **73**, 368; ibid., 1949, **74**, 2
9 *Perfum. essent. Oil Rec.*, 1948, **39**, 286
10 *Soap, Perfum. Cosmetics*, 1949, **22**, 1232
11 Ibid., 999
12 Ibid., 368

[13] *Amer. Perfum.*, 1948, **52**, 321
[14] *Analyst*, 1949, **74**, 397
[15] *Lebensmitt. Untersuch. Hyg.*, 1947, **38**, 292
[16] *Chem. & Ind.*, **1949**, 767
[17] *Soap, Perfum. Cosmetics*, 1949, **22**, 712
[18] *Ind. Eng. Chem. (Anal. Ed.)*, 1940, **12**, 479
[19] *Mfg Chem.*, 1948, **19**, 542
[20] Ibid., 443
[21] *Amer. Perfum.*, 1949, **53**, 121
[22] *Soap, Perfum. Cosmetics*, 1949, **22**, 848
[23] U.S.P. 2,435,005
[24] *J. Soc. cosmetic Chem.*, 1948, **1**, 109
[25] *Beauty Aids*, 1949, **2**, 14
[26] *J. Soc. Dy. Col., Bradford*, 1949, **65**, 447
[27] *Drug Cosmetic Industr.*, 1949, Sep., 264 ; *Lancet*, **1949**, 707
[28] *Hairdressers J.*, **1949**, 17
[29] U.S.P. 2,479,382
[30] *J. Soc. Dy. Col., Bradford*, 1949, **65**, 447
[31] Ibid., 1948, **64**, 305
[32] *Research*, 1949, **2**, 246
[33] *J. Soc. Dy. Col., Bradford*, 1949, **65**, 390
[34] *Nature*, 1949, **164**, 576
[35] *Amer. Perfum.*, 1949, **53**, 207
[36] *Hairdresser Beauty Tr.*, **1949**, 11
[37] *Drug Cosmetic Industr.*, 1949, **64**, 37
[38] *Hairdressers J.*, **1949**, 41
[39] *Chem. & Ind.*, **1949**, 704 ; *Nature*, 1949, **164**, 563
[40] *Perfum. essent. Oil Rec.*, 1949, **40**, 323
[41] Evans, R. L., B.P. 593,438
[42] *Soap, India*, 1948, **1**, 11
[43] *Mfg Chem.*, 1948, **19**, 497
[44] *Perfum. essent. Oil Rec.*, 1949, **40**, 331
[45] Ibid., 168
[46] Ibid., 48, 54
[47] Ibid., 14
[48] *Soap, India*, 1948, **39**, 8
[49] Ibid., 1948, **39**, 386
[50] Ibid., 1949, **40**, 395

PLASTICS

BY MEMBERS OF THE PLASTICS GROUP

POLYMERIZATION PRODUCTS (J. W. C. Crawford, B.Sc., Ph.D.)

THE period has shown maintained interest, academic and technical, in subjects connected with polymers and polymerization. Study of polymerization processes continues to be directed towards a better understanding of the steps involved in them, and towards measurements of rate constants with increased accuracy. Increased realization appears of the technical importance of chain transfer in the polymerization process. A number of new polymerization catalysts have been introduced and studied ; most outstanding perhaps is the class of the azonitriles. New methods of obtaining information on the dimensions of macromolecules have been suggested or are under investigation, and intermolecular relationships, determinative of the properties of polymers, especially the mechanical properties, have been investigated rheologically and otherwise.

The ion-exchange and other electrical properties of polymers or copolymers containing strong electrolytes (ammonium ions) covalently bound in the macromolecules have been examined. A kindred and interesting investigation is the examination of the alteration of macromolecular dimensions of copolymers containing acid groups with change in p_H, showing perhaps some affinity with muscular action and providing possibly a route to conversion of chemical to mechanical energy. Polymers containing vinylhydroquinone showing electron-exchange properties have been prepared.

On the technical side, considerable interest has been shown in the possibilities of low-temperature polymerization as affording polymers of increased linearity. Work is at present mainly in the field of synthetic rubbers, where attainment of more linear polymers is a matter of much importance in improvement of mechanical properties, and has been carried out with both free-radical and ion-initiated polymerization systems.

American information shows that production of the major types of plastic has now caught up with demand, with the exception of polyethylene. Of technically new polymers undergoing development, mention may be made of polytrifluorochloroethylene, of quick-curing alkyd resins showing high electrical tracking resistance, and of the new fibre of outstanding properties based on polyacrylonitrile.

Processes

Free-radical polymerization ; catalysis

The possibility of measuring rate constants of free-radical polymerizations from measurement of magnetic susceptibility of the system has been examined by P. W. Selwood.[1] At present the susceptibility of the

best magnetic balances is still several orders away from detection of the free-radical concentrations estimated to be present in polymerizing ethenoid systems.

In a polymerizing system the active centres are present in small concentration. R. N. Haward[2] calculates that if the system were subdivided into drops until on the average each drop contained only one active centre, the drops would be of colloid dimensions (10^{-4}–10^{-5} cm.), and large in comparison with a monomer molecule; it is further concluded that in practical emulsion-polymerization systems, droplets containing only small numbers of reacting molecules may form. It is calculated that the generation singly of active centres in the isolated drops would then lead to increase of rate of reaction and molecular chain length as the drop size diminished; where the active chains are formed in pairs, the opposite would be expected, i.e. decrease in reaction rate and chain length. High rates of reaction and chain lengths observed in emulsion- as compared with bulk-polymerization agree with the calculations for single generation, and on the other hand reduced reaction rate is apparently never observed in emulsion systems.

The general discussion by W. V. Smith and R. H. Ewart[3] of the kinetics of emulsion-polymerization has been followed by a examination by W. V. Smith[4] of conditions in emulsion-polymerizing styrene. According to Smith and Ewart, the radicals formed by reaction between persulphate catalyst and styrene monomer dissolved in the water practically all enter either soap micelles or polymer particles, and continue polymerization of monomeric styrene there. Growth of polymer particles increases the amount of soap adsorbed at their surfaces until finally all the soap is thus disposed and no more micelles remain. At this point substantially no new particles will form, and it is shown that the rate of polymerization will be substantially uniform and based on the unit particle until the separate styrene phase disappears, after which the rate will fall away. It has been shown experimentally that styrene can be polymerized in persulphate solutions seeded with polystyrene particles substantially without altering the number of particles; that (at lower concentrations of particles) the rate of polymerization per particle is substantially constant, and independent of the size of the seed particles. Over a 16-fold variation in persulphate catalyst concentration, the rate of polymerization per particle is independent of persulphate concentration. The interpretation is that the average number of free radicals per particle is constant and equals one-half. From the rate of polymerization per particle and concentration of monomer in it the chain propagation constant has been calculated. Factors favouring production of a large number of particles are high soap and persulphate concentrations and high temperatures.

It has been maintained by Fordyce and his co-workers that experimental results indicate that the propagation of polymerization in an emulsion system occurs almost entirely in the non-aqueous phase. This argument rests on the smaller content in the copolymer of the more water-soluble component when emulsion polymerization is used than in bulk polymerization products from the same monomer mixture, the more water-soluble component being partially extracted from the oil disperse phase by the water, and not participating in the propagation reaction.

Further support for this view has been obtained by R. G. Fordyce and G. E. Ham[5] from emulsion copolymerizations of styrene with acrylontirile, in which the water–monomer phase ratio was varied between 2 and 20 : 1. Acrylonitrile in the water phase was calculated to be 2·1–0·8 g./100 ml. Analysis of copolymer at early stages in the copolymerization showed a reduction of acrylonitrile corresponding to reduction of monomer in the oil phase by water extraction as the proportion of water phase rose; further, since the true solubility of styrene in the water phase was very low (0·06 g./100 ml.), the composition of the copolymer indicated that little, if any, of it was formed in the water phase. The nature of the emulsifier used had no effect on the composition of this copolymer.

If in the high-pressure (5000 atm.) polymerization of ethylene, the reaction temperature is kept below the softening point of the polythene (below 100° c.), it is possible to wash the polymer out of the reactor by a stream of water running over the walls of the vessel.[6] Diethyl peroxydicarbonate (EtO·CO·O·O·CO·OEt) will initiate the polymerization at these temperatures; the water used to remove the polymer is recycled. Inhibiting effect of oxygen is noted, and more than 0·5% of propylene in the monomeric ethylene will lower the softening point of the polymer. Surface-active agents may be present in the scrubbing water.[7]

Low-temperature emulsion-polymerization of butadiene–styrene mixtures is reported on by C. F. Fryling, S. H. Landis, W. M. St. John and C. A. Uraneck.[8] It has been known for some time that polymerization of these co-monomers at low temperatures gave rubbers of improved mechanical properties, owing possibly to the effects of increased 1 : 4-polymerization of the butadiene, but with conventional recipes the polymerization process was impracticably slow. The paper deals with the development of emulsion-polymerization recipes giving rapid polymerization at temperatures which may fall below freezing point. Improved activators are the main contribution, and include the diazothioethers (with potassium ferricyanide as accelerator), and redox activators based on organic peroxide (cumene hydroperoxide)–iron pyrophosphate–reducing sugar systems; if the iron is present in the ferrous form, the sugar may be omitted. *tert.*-Alkyl mercaptans play an important part as modifiers, and on account of the operating temperatures, freezing point depressants for the aqueous phase must be supplied. Increased linearity of the butadiene–styrene copolymer molecules is an important feature of the low-temperature emulsion-polymerization process,[9] and leads to improved properties of the rubber; an increased tendency to crystallize and give poorer low-temperature behaviour is offset by introducing into the copolymer a proportion of a diene having a side-chain, such as isoprene. The proportion[10] of 1 : 2-addition of diene falls slightly (by 2–4%, from 23% at 50° c.), and the proportion of trans- 1 : 4-units increases greatly with fall in polymerization temperature, from 50% at 100° to 80% at − 20° c. The styrene co-monomer does not affect these changes.

Non-monomer phases other than water have been investigated.[11] Sequestering agents for ferrous ion other than pyrophosphoric acid have been found, and non-ferrous activators have been investigated.[12]

The ability of slow neutrons to rupture chemical bonds (Szilard–Chalmers effect) has been utilized by Y. Landler and M. Magat[13] to

induce polymerization. When styrene containing ethyl bromide is bombarded by slow neutrons, it polymerizes by virtue of initiation by ethyl radicals resulting from break up of the C_2H_5 Br* produced by capture of neutrons by the bromine: most of the polymerization, however, derives from effects secondary to the Szilard–Chalmers.

Thermally activated polymerization of styrene in magnetic fields of 40,000 and 8000 gauss at 100° and 80° C. (air absent) shows that the magnetic field does not inhibit polymerization or affect the intrinsic viscosity of the polymer.[14]

In the emulsion polymerization of vinyl chloride, reaction rate accelerates to a maximum at 80–85% conversion and after a period of constancy falls off rapidly. By altering the reaction temperature (through the range 70–40° C.) variations in rate can be compensated for. This treatment is claimed to reduce the time for polymerization by 40–50%, enables the dispersing or emulsifying agent to be reduced by 25% or more, and gives a much smaller polymer particle size with a uniform mean molecular weight throughout the reaction. Less hydrogen chloride is produced by decomposition of polymer.[15] In order to obtain an emulsion-polymerized latex of polyvinyl chloride (or vinyl–vinylidene chloride copolymer) with maximum stability on storage, it is considered[16] that the particle diameters of the suspended polymer should lie between 500 and 3000 A. It has been found that if a proportion of a polymer latex be added to an emulsion-polymerization system based on vinyl chloride formation of fresh polymer occurs on the added polymer particles rather than at fresh *loci*. This makes it possible, by suitable adjustment of added polymer and fresh monomer in the system, to grow particles in the required range of diameters to give the most stable latices; the polymer used to 'seed' the latices is prepared in a straight monomer polymerization, so as to give particles of diameters lower than desired.

Because of the insolubility of polyvinyl chloride in its monomer the monomer retains its low viscosity in mixtures of the two; this makes possible dilatometric measurement of the rate of polymerization. This has been done by W. I. Bengough and R. G. W. Norrish[17] for vinyl chloride at 47° C. catalyzed by benzoyl peroxide. Previously Prat[18] had found an acceleration of rate of polymerization over the first 40%. This acceleration has been separated by Bengough and Norrish from the possible retarding influence of impurities, and confirmed; it has been shown to be associated with the presence of polyvinyl chloride, but only if it is present as solid, and if benzoyl peroxide catalyst is also present. The rate of polymerization increases with added polymer proportionally to the amount of polymer present. The explanation is that transfer occurs between free radicals in solution and the solid polymer; this gives on the surface of the solid immobile radicals that are free from the tendency to self-neutralization possessed by radicals in solution, and therefore more effective for producing initiation of polymerization. The number of such surface radicals will be proportional to the surface of the solid polymer; the technical importance of this observation is pointed out in relation to build-up of polymer in plant.

The rate of initiation in the polymerization of vinyl acetate has been measured by (*a*) using azo-bis*iso*butyronitrile as thermal initiator and

taking the rate of initiation as twice the rate of decomposition of initiator and (*b*) using benzoquinone as inhibitor and assuming that two quinone molecules stop two polymer chains; the results of the two methods agree. From them and from kinetic chain lifetimes, rate constants and activation energies for chain propagation and termination have been calculated.[19]

C. H. Bamford and M. J. S. Dewar[20] have studied the ultra-violet-photoactivated polymerization of methyl methacrylate by a viscosimetric method described by them earlier[21] giving absolute velocity constants for the polymerization. The thermal polymerization is a normal radical chain process, with constants evaluated for reaction at 0° C. In the case of the ultra-violet photoactivated process, irreproducibility of the viscosity rates led to an investigation of causes of interference, from which it was concluded that ultra-violet light produced a catalyst, whereas in the thermal reaction an inhibitor is formed. Reactions are suggested for formation of such substances from the methacrylate monomer; their presence would account for difficulties experienced by other workers, and would explain the anomalous polymerization observed by Melville[22] and put down by him to an 'activated double bond,' non-terminating polymerization.

The average lifetime of growing polymethyl methacrylate radicals in photoactivated polymerizing monomer has been measured[23] as a function of temperature, and the data combined with Schulz's data on rate of polymerization and molecular weight as functions of initiating free radical concentration to give the rate constants of the propagation, termination and transfer reactions. Up to at least 10% conversion, the termination rate constant is probably independent of polymer chain length, but the accelerated polymerization rate in later stages of the conversion is due to a decrease in the value of the constant.

K. Ziegler[24] considers the stability of the radicals generated on dissociation of aryl-, arylalkyl-, and alkyl-ethanes from the view points of resonance and of strain on the ethane C–C bonds due to the substituents. The action of the radicals in initiating polymerization of ethenoid compounds is discussed. Note is made of the usefulness of acrylonitrile—whose polymer is completely insoluble in the monomer—as a gauge of the speed of dissociation of a parent substance into free radicals, by observation of time for commencement of turbidity. Dilatometric measurement of rate of polymerization of acrylonitrile catalysed by radical-producing substances gives half-life times in good agreement with the values calculated from the dissociation velocity constants measured by reaction of the radicals with such reagents as iodine, nitric oxide, or tetrachloroquinone.

L. Horner[25] has followed analytically the fate of acetylsalicylyl peroxide used to catalyse polymerization of styrene; according to theory, the fragments of the peroxide should be built into the polystyrene. Alkaline saponification by a special method shows that about 75% of the peroxide reacts with the monomer to form salicylic ester-groups. About 12% reacts to form ketone groups (analytically estimated); about 12% of double bonds are found by oxidation and bromination analyses, and these double bonds are terminal: they correspond with the free acid in 1 : 1 ratio, this resulting from an *R*H reaction of benzoyloxy radicals

with monomer. Less than 2% of peroxide goes to phenyl acetate, and carbon dioxide evolved in the reaction corresponds with the extent of the phenyl acetate and ketone group producing reactions ; end group calculations of molecular weight agree with cryoscopically determined figures. Reaction mechanisms are given in this summarized statement ; termination on peroxide molecules is accepted, with further initiation of a polymer chain by the residual radical formed after termination with ester group formation.

Many amines will activate peroxide-catalysed polymerization ; G. S. Whitby and N. Wellman[26] show that polyalkylene polyamines added to an emulsion-polymerization system containing organic hydroperoxide catalyst greatly increase the rate of polymerization.

The interpretation of the absorption spectra of such ion pairs as $Fe^{+++}OH^-$ as electron transfer spectra, e.g. $Fe^{+++}OH^- \rightarrow Fe^{++}OH$ (Rabinowitch, 1942), receives experimental support from the finding of M. G. Evans and N. Uri[27] that ethenoid monomers (acrylonitrile, methyl methacrylate, styrene) will polymerize on irradiation of their solutions with light of wavelength less than 3000 A. in presence of $Fe^{+++}OH^-$; the polymerization is initiated by hydroxyl formed by the photochemical reduction of the Fe^{+++}. Photopolymerization in dilute ferric salt solution is practically suppressed in strongly acid medium owing to the minimal concentration of $Fe^{+++}OH^-$ present. $Fe^{+++}Cl^-$ ion pair gives with methyl methacrylate a polymer, mol.wt. 20,000, containing chlorine ; molecular weight of the polymer calculated from the chlorine content on the basis of one chlorine atom per molecule agrees with the figure obtained viscosimetrically.

The action of aliphatic azonitriles in initiating polymerization of ethenoid compounds is due to their ready decomposition on heating into nitrogen and free radicals ; e.g. 2 : 2′azo-bis*iso*butyronitrile, $Me_2C(CN){\cdot}N_2{\cdot}C(CN)Me_2$, gives $Me_2C(CN)$ radicals. A number of such azonitriles based preparatively on methyl-alkyl ketones, and also on *cyclo*hexanone, have been prepared, and their rates of decomposition in toluene solution at 80° c. measured. All give first-order rate constants. Activation energies have been calculated using these and the rates at 70° c. Variation in rate constants is not thought to be due to hyperconjugation or inductive effects of the alkyl groups, and steric effects are called in for an explanation. The rate of decomposition is essentially independent of the nature of the solvent used ; this, with the formation of tetra-alkyl succinonitriles as reaction products, and the initiation of ethenoid polymerization by the decomposing azonitriles, supports the view of the reaction involving the formation of free radicals.[28]

The question whether the sodium-produced polymerization of butadiene and isoprene is due to the addition of diene to an initial diene–disodium addition compound, or whether it is a free-radical polymerization initiated by the radical result from addition of an atom of sodium to a molecule of diene, has been investigated by R. E. Robertson and L. Marion.[29]

Ion-initiated polymerization

D. D. Eley and A. W. Richards[30] have investigated the kinetics of polymerization of 2-ethylhexyl vinyl ether in solution at 25° c. under

catalysis by iodine, stannic chloride, silver perchlorate and triphenylmethyl chloride. Positive-ion initiation is the explanation of the catalytic action; iodine operates by forming I^+ and I_3^-; the I^+ with monomer forms the initiating carbonium ion. Triphenylmethyl chloride, largely ionized in the solvent used (*m*-cresol), initiates polymerization by action of Ph_3C^+ on monomer. Because the coordination number of tin is six, it is considered that $SnCl_4$ may start two chains, from $M^{+-}SnCl_4{}^-M^+$; this is consistent with the markedly higher molecular weights found for polymers made with this as compared with the other catalysts. Water has a specific effect on the polymerization; with stannic chloride the rate is unchanged, with silver perchlorate it is accelerated. This it is suggested is due to the special reaction:

$$H_2O.AgClO_4 + \underset{\displaystyle CH}{\overset{\displaystyle OR}{|}} = CH_2 \rightarrow {}^{+}\underset{\displaystyle CH}{\overset{\displaystyle OR}{|}} - CH_3 + HOAgClO_4^-.$$

The existence of transfer reactions is discussed.

Sodium amide-catalysed polymerization of styrene in liquid ammonia is reported by J. J. Sanderson and C. R. Hauser.[31] The low molecular weight (3000) product was similar in properties to a polymer prepared by thermally activated polymerization at 240° C.; an ionic mechanism is suggested. Methacrylonitrile is an especially interesting subject[32] for anion-initiated polymerization because of the presence of the highly electronegative cyano group which facilitates nucleophilic attack, and the absence of an α-hydrogen atom which might cause early ending of the growing polymer chain by chain transfer. Experimentally it is found that methacrylonitrile will polymerize readily under the influence of a number of basic catalysts, and, especially with sodium in liquid ammonia at − 75° C., molecular weights of over 10^5 can be reached. Evidence is produced to show that the polymerization is ionic in nature.

The low melting points and poor solvent power of fluorocarbons have led to their trial as non-monomer phase in low-temperature (− 70° C.) emulsion-polymerization of *iso*butylene or *iso*butylene–butadiene, catalysed by boron fluoride. Trouble was experienced with coagulation (no soluble emulsifying agent could be found), but butyl rubbers of satisfactory properties were obtained.[33]

Chain transfer

Chain transfer experiments in the polymerization of styrene in presence of a series of mercaptans show that the latter have a high reactivity towards radicals in supplying a hydrogen to them in the transfer reaction. The reactivity is reduced by α-substitution of methyl in the mercaptan and increased by α-carbethoxy substitution.[34] Pure chain transfer affects the speed of polymerization of ethenoid compounds[35] only when the polymers formed are of low order (up to e.g. decamers), even when the new nucleus forms slowly. The marked decrease in rate of polymerization of vinyl acetate with increasing dilution by benzene, toluene, or chlorobenzene can be explained by a chain transfer which results in increased chain termination by the radicals formed from the solvent.

The gelling of polyethenoid monomers at a comparatively early stage in their polymerization could be overcome[36] by reducing the chain length of the polymer molecules so as to delay the attainment of 'infinite' molecular weight networks. The polymerization of allyl methacrylate has been studied in this sense by S. G. Cohen and D. B. Sparrow by adding to the monomer–benzoyl peroxide catalyst system substances likely to be inhibitors, retarders, or chain-transfer agents. Amongst these, thiols showed the desired effect and were studied further. It has been shown that all of a series of six thiols increased the polymer concentration at the gel point; thioglycollic acid in concentration 0·043 mol./l. gave a polymer concentration of 28% at the gel point, as against 6% in its absence; rates of polymerization were slowed down. In experiments with methyl methacrylate, thioglycollic acid slowed down the rate of polymerization and reduced the molecular weight of the polymer by 53%. Determination of unsaturation was carried out on soluble polyallyl methacrylate under conditions (bromide–bromate titration) in which the allyl group would consume 97–98% theoretical bromine, the methacrylate only 45%. It was found that the soluble polymer absorbed 96–97% theoretical bromine whether made in presence of thioglycollic acid or not; it was concluded that very little methacrylate unsaturation remained.

Copolymerization

Addition copolymerization is discussed by R. Simha and L. A. Wall.[37] Aspects considered are: quantitative treatment of the reaction involving initiation, growth, and termination; analysis of copolymers; reactivity ratios, with tabulated data; degradation of copolymers, with derivation of a ratio between yield and copolymer composition. Outstanding problems are enumerated.

The chemical composition[38] of a copolymer depends mainly on the various chain-propagation reactions; over-all composition and distribution of monomer sequences in the molecule can be calculated in terms of monomer concentrations and rate constants. Monomers having substituents on both ethylene carbon atoms do not readily add to themselves in growing chains, but can copolymerize with CH_2:C> compounds. Reactivity of monomer is governed largely by the resonance stability of the radical adduct and the polarity of the double bond. A semi-quantitative treatment is given of reactivity determined by the resonance effect. The copolymerization studies of Price and Alfrey, and of Mayo and his colleagues, have shown that free radicals and monomers show significant differences in reactivity. In this general connexion, M. G. Evans, J. Gergely and E. C. Seaman[39] discuss the activation energy of radical–monomer reactions in terms of bond energies and repulsion energies between reacting centres. For a number of simple prototype reactions it is found that the heat of reaction is a most important factor in determining the activation energy; this result is extended to a wide variety of substituted radicals and monomers. Variation in the heat of reaction is expressed in terms of resonance energies of the reacting radicals and monomers. The repulsion energy factor is important and is affected by charge distribution on the reacting centres and steric effects of substituents.

The effect of the latter on the charge distribution is discussed by the molecular orbital method.

In the copolymerization of *o*-chlorostyrene with anethole (*p*-methoxy-β-methylstyrene), copolymers much richer in anethole were obtained when an ionic catalyst (stannic chloride) was used than with free-radical initiation by benzoyl peroxide. It is concluded that the steric effects that are supposed to hinder reaction of 1 : 2-disubstituted ethylenes with polymer radicals are much less apparent when polymerization proceeds through a carbonium ion.

Molecular size

The electron microscope has been used[41] to determine the molecular weight of highly polymerized styrene ($\sim 10^6$ mol. wt.). The polymer is deposited on collodion substrate from extremely dilute solution, and forms minute spheres of approximately 2 μ. radius. Contrast is brought up by shadowcasting with 3 A. of uranium to enable dispersion of single particles to be observed. Molecular weights calculated from the results obtained agree with osmotic values, when the particles are assumed to be single macromolecules.

On the basis of Guggenheim's theory of solutions of macromolecular substances, E. Kunst and M. Magat[42] have calculated the effect of branching on the osmotic pressure. Theoretically, indications of the degree of branching should be obtainable by comparison of macromolecular substances differing only in degree of branching, but in practice the errors in measurement would exceed the differences, unless the difference in degree of branching was very great.

Measurement of the surface pressure of dilute solutions of macromolecular substances, from which the molecular weight may be calculated from a modified Boyle's law ($PS = RT$, where S is the surface occupied by a g.-mol.), has been carried out by M. Abribat and J. Pouradier[43] using instead of the micromanometer used previously, the Dognon–Abribat matt-film tensiometer. The molecular weights of a number of macromolecular substances examined are in good agreement with osmometric values.

R. D. Andrews, N. Hofman-Bang and A. V. Tobolsky[44] have studied the relaxation of stress in poly*iso*butylene over a range of molecular weights and temperatures (30–100° C.), and at different elongations. The activation energy for relaxations is independent of molecular weight in the range studied. The relaxation rate depends on molecular weight with such sensitivity that relaxation measurements may be a practical method of measuring the molecular weight directly in the solid state.

Plasticization

R. F. Boyer[45] discusses the inter-relation of three aspects of plasticizer properties *vis-à-vis* the polymer: compatibility, in terms of the Flory–Huggins treatment of polymer–solvent thermodynamics; efficiency, the relative power of a plasticizer to lower the brittle temperature (empirically related to the Huggins interaction constant); and permanence, the ability of plasticizer to remain in the polymer on ageing or heat-treating (this depends on the effective vapour pressure of the plasticizer

and on the diffusion rate of the latter from the interior of the plasticized polymer). Diffusion rates can be correlated with plasticizer content and efficiency, and with brittle temperature. A plasticizer of high efficiency can diffuse out relatively rapidly from the polymer. Polymeric plasticizers are briefly discussed with reference to the above three aspects.

The molecular weight, size and shape of plasticizers is of importance in determining plasticizing effect.[46] The Huggins constant μ can be taken as a measure of the binding force between polymer and plasticizer. A low μ means strong bonding and good cold resistance of the plasticized polymer. At a value of less than 0·25 μ falls further with falling temperature. Increase in 'solvent power' of a plasticizer on cooling is taken as a criterion for plasticizers giving good cold resistance. Extraction experiments with mineral oil on plasticized polyvinyl chloride–acetate copolymer shows that the best plasticizers for cold-resistant compositions are easiest extracted. Plasticizing action depends on two different mechanisms: at the basis of one is the molecular weight of the plasticizer; the other depends on the ability of polar plasticizers to form associations with active parts of the polymer, varying in definiteness between statistically conditioned swarms to definite molecular compounds. The favourable influence of reduced temperature on formation of associations is in agreement with the observations on μ, and with Doolittle's 'solvent power' observations. The second mechanism is dominant at low temperatures, and becomes subordinate to the first at elevated temperatures. The easy extractability of good low-temperature plasticizers is due to breaking up of associations by solvent.

Testing and properties of plastics

E. C. Bernhardt[47] discusses the variables involved in scratching a material with a hard tool, and concludes that scratch resistance, independent of depth of scratch and thus of load on the tool, is expressible as the tangential force necessary to propagate the scratch along the surface of the (rotating) test material per unit cross section of scratch, provided that the material is homogeneous; these conclusions were reached with the aid of a special instrument, which is described. Experimental findings are discussed with reference to the types of abrasion met with in usage of plastics. H. J. Green, junr.[48] describes experiments on the continuous measurement of rate and amount of moisture absorption of plastic materials in an apparatus in which the moisture taken up, as well as the electrical resistance of the specimen, may be measured without its removal. Moisture is absorbed from an atmosphere of 97% humidity at 30° C. It is shown that under these conditions a straight line relationship is shown by a log–log plot of % moisture absorption against time, up to saturation point. This fact reduces the number of observations to be made in assessment of a given material. Using a refractometric method developed earlier by himself (Abbe refractometer with resin in film form) R. H. Wiley[49] has observed the second-order transition temperatures of a number of polymeric acrylic and methacrylic esters. The temperature for polymethyl acrylate is 0° C.; polymethyl methacrylate, 72° C. Birefringent effects are shown by polymers of long-chain alkyl esters below the transition temperature.

The compressibility of a number of plastics has been investigated at pressures up to 100,000 kg./cm.^{2} by P. W. Bridgman.[50] Although initial compressibilities vary considerably, the differences tend to disappear as pressure rises. The p/v relationships were all smooth with the exception of polytetrafluoroethylene which showed a discontinuity at $p = 6500$ kg./cm.^{2} indistinguishable from an ordinary reversible polymorphic transition.

W. G. Oakes[51] has measured the intrinsic electrical strengths of polythene, polystyrene, poly*iso*butene, polymethyl methacrylate, chlorinated and oxidized polythene over the temperature range $-200°$ to $+110°$ c. The electric strengths of the non-polar polymers, polythene, polystyrene, poly*iso*butene vary little at low temperatures. At above about 40°, 90° and $-50°$ c. respectively the electric strength falls rapidly with rise in temperature. The polar polymer, polymethyl methacrylate, has much higher electric strength than the non-polar polymers at low temperatures, falling off gradually with rise in temperature to about 20° c., after which the fall is considerably more rapid. Chlorination of polythene tends to increase in the electric strength at low temperatures, decrease at high temperatures, and a lowering of the point of inflexion of the temperature–electric strength curve: oxidation of polythene gives a higher low-temperature electric strength. The results are discussed in the light of Fröhlich's theory of breakdown.

In a study of the adhesion of high polymers to cellulose, A. D. McLaren[52] demonstrates that adhesion of high polymers to cellulose is a function of 'tack temperature' of the polymer (the temperature at which the polymer has approximately a standard viscosity), its dielectric constant ϵ, and dipole moments μ of polar groups present. A plot of tack temperature against 'mirror image force' (μ^2/ϵ for a simple polymer; $\mu_1 \mu_2/\epsilon$ for a copolymer, μ being taken as the same as present in the monomer) gives an area of relatively high adhesion below the tack temperature of 100° c. and $\mu_1 \mu_2/\epsilon$ values 0·7–1·3, extending outwards as tack temperature falls. Outside this area adhesion of polymer to cellulose is poor. By coating polymers on cellulose pretreated with Werner chromium complexes of acids bearing polar groups, it has been found that adhesion is a specific function of the polar groups within the polymer and on the modified cellulose. Adhesion is strongest with approximately equal dipole moment substituents in the modified cellulose and in the copolymers.

The incompatibility or demixing of solutions of macromolecular substances in solution has been investigated by Mmes. A. Dobry and F. Boyer-Kawenkoi.[53] Solutions of high polymers, dissolved in the same solvent, may on mixing produce a turbidity, resolved on standing into two separate layers, in each of which one of the polymers is the major constituent. Demixing is a process reversible on dilution. About 20 substances have been tested in binary mixtures, with a variety of solvents; included are some water-soluble high-molecular substances. The following generalizations are brought out for organo-soluble substances. Compatibility—absence of phase separation over the complete range of concentration—is exceptional, only 4 out of 34 pairs of substances being compatible; if high polymers are compatible in one solvent, they are usually so in all others; the concentration limit at which demixing occurs

depends on the solvent; the molecular weight of the high polymers is important in determining the demixing limit—the higher the molecular weights, the less the compatibility. It seems possible that even more than molecular weight, molecular shape may influence the mixing; branch-chain polymers undoubtedly do not have the same demixing limits as straight-chain. There is no obvious relation between the compatibility of two high polymers and their base-molecular structure. A similar main-chain structure does not ensure miscibility. General agreement with the findings of the above workers results from the thermodynamic analysis of the two polymer–one solvent system by R. L. Scott.[54] The same author, following a calculation of the phase diagrams of a two solvent–one polymer system, concludes[55] with relation to the solubility of polymers in liquids, that beside the cases of two solvents, and one solvent–one non-solvent for the polymer, complete solution of the polymer may occur in a mixture of two non-solvents, provided that the cohesive energy density of the polymer is between those of the two liquids, if they are themselves miscible.

P. Debye and A. M. Bueche[56] have examined the thermal diffusion of high polymer solutions using a Clusius thermal diffusion column. High polymers have been shown to have a fairly large thermal diffusion effect; since thermal diffusion separation is dependent on molecular weight, it is suggested that a method of polymer fractionation is present here.

The coiling and uncoiling of ionizable linear-macromolecular substances (polymethacrylic acid) is under examination by W. Kuhn, O. Kunzle and A. Katchalsky.[57] The macromolecules, normally coiled in aqueous solution, straighten out when alkali is added, because of electrostatic repulsion between the carboxyl ions produced; this straightening produces changes in the physical properties of the solutions. In the present paper, the effect on viscosity is recorded. The intrinsic viscosity increases greatly as the polymeric acid is neutralized by alkali. Calculations are made of the effect of degree of ionization on the intrinsic viscosity and good agreement is shown with the experimental results. The large change in distance between the ends of molecules of polymethacrylic acid on addition of small amounts of alkali is emphasized and a possible parallel is suggested with the view that muscular contraction is due to change in form of the molecules of the fibrous proteins. A brief note has appeared[58] concerning work of a similar nature being done at the Weizmann Institute; a methylvinylacetic acid polymer rubber is the working material, and its variations in dimension on successive contacting with acid and alkali are employed to do mechanical work. The note suggests the attainment of a higher efficiency, presumably compared with a heat engine.

Applications of plastics

B. J. Hogg and H. E. Duckworth[59] have examined the suitability of a number of synthetic dielectrics for vacuum applications, in terms of the effect vapours arising from them have on the vacuum obtainable in a standard system. Teflon (polytetrafluoroethylene), was excellent in this respect, showing negligible vapour pressure; polystyrene and polyethylene were also good. A description has appeared of the application of corrugated plastic sheet in roof and side-lighting of corrugated iron buildings.[60]

The plastic, formed to corrugated sheet of the same frequency and amplitude as the iron, is slipped in under or over neighbouring metal sheets and screwed in place on the frame members just as for corrugated sheet itself. Use of this method avoids construction of expensive metal sashes necessary when glass lights are used. The toughness of the plastic compared with glass is an additional advantage, although its first cost is higher; elimination of sash costs and replacements is therefore considered to make the use of corrugated plastic attractive economically. Plastics used are polymethyl methacrylate, and glass fibre mat bonded with polyester plastic.

Individual polymers

Olefine polymers

D. W. Bird and H. Pelzer[61] have measured the intrinsic electric strength of polythene: by quenching or slow cooling of the hot specimen, crystallite dimensions were varied over a wide range; no significant differences in electric strength were found. An optical lever micrometer for measuring the thicknesses of the (readily deformable) specimens is described. Heat of combustion data for polythene[62] lead to the conclusion that the polymer is crystalline to the extent of at least about 50% at 25° c. Using a microphotometric method of comparison of *X*-ray intensities, J. L. Matthews *et al.*[63] obtained indications that the amorphous content of polythene samples may range at room temperature from below 10 to above 50%, normal samples having around 25%.

E. Hunter and R. B. Richards[64] make use of the considerable solubility of polythene in ethylene, or other gaseous hydrocarbon under conditions of high pressure and elevated temperature, to fractionate the polymer into portions of differing mean molecular weight. This is done by partial reduction of temperature and/or pressure of the polythene-hydrocarbon gas solution, when higher molecular weight species are first deposited.

R. G. Newberg, D. W. Young and H. C. Evans report[65] tests on blends of polythene with poly*iso*butylene: mechanical performance, permeability, chemical-, light- and heat-resistance; they consider that for ease of fabrication, poly*iso*butylene of molecular weight 120,000 is preferable to lower (80,000) or higher (260,000) molecular weights. Applications of polythene in surgery include packing the cavity left in a patient's chest after lung collapsing with a polythene tape-filled polythene film bag,[66] and as a substitute for human bone in reconstructive surgery.[67] In both cases, the inertness of the polythene towards body tissues is a valuable property, enabling the material to be left in the body for long periods, possibly permanently, without setting up irritation.

Vinyl*cyclo*propane made in 1922 by Demjanow and Dojarenko is suggested[68] as an interesting material for polymerization studies; the polymers may differ considerably from those of the isomeric isoprene and piperylene.

Polystyrene

*iso*Propylbenzene can be catalytically dehydrogenated[69] to give α-methylstyrene in practicable yields, employing oxide catalysts, and

with or without the presence of steam; a small amount of styrene is simultaneously formed. Non-catalytic dehydrogenation can be operated (at 700° c.) to yield mainly styrene (ultimate yield less than 60%).

Polystyrene undergoes degradation[70] on exposure to light of wavelength 2537·5 A.; the rate of degration is proportional to the first power of the incident light. Rheological studies of polystyrene relating to the phenomenon of 'crazing' are reported by B. Maxwell and L. F. Rahm[71] and by J. A. Sauer, J. Marm and C. C. Hsiaio.[72] Elimination of age-crazing from styrene is claimed by Monsanto Chemical Company and R. F. Hayes[73] if the sodium salt of dioctyl sulphosuccinate is incorporated in small amount in the styrene, followed by a suitably long heat treatment.

Molecular dimensions of polystyrene fractions have been obtained from viscosity and light scattering data. Root mean square distance between the ends of the molecule approximates to the diameter of the molecular sphere needed for the explanation of viscosity. Evidence was obtained for absence of appreciable branching or cross-linking in the styrene fractions (thermally polymerized at 100° c.). The polystyrene molecules in benzene solution are much stiffer than corresponds to a free-rotation molecule, and this explains the relatively high viscosities of polystyrene solutions.[74]

Ion-exchange materials are made from polystyrene (DP $>$ 1000) by conversion, through normal reactions with the aromatic nuclei, to diazonium salts which are coupled with suitable phenolic substances or aromatic amines.[75]

Polyvinyl chloride

Colour develops in polyvinyl chloride when it is exposed to such high temperatures as are used technically in its processing. The polymer has been shown to have a head-to-tail arrangement of monomer units in the macromolecules. Marvel and his co-workers have shown that treatment of polyvinyl chloride with alkali removes the chlorine as hydrogen chloride, the polymer becoming progressively more deeply coloured during the treatment until it is finally reddish-brown. This colour change is closely paralleled when polyvinyl chloride is heated above 100° c.; hydrogen chloride is likewise evolved during the heat treatment. It is concluded that polyene structures . . . $-CH = CH - CH = CH - CH = CH-$. . . are formed in the macromolecules by both treatments, the colour intensity increasing with length of polyene runs; this has been demonstrated by Kuhn and co-workers for a variety of polyenes of known structure. Measurement of the light transmission of thin moulded polyvinyl chloride disks[76] shows absorption peaks at about 4000–4600 A., increasing with continued heat treatment; such peaks are shown by carotene-like (polyene) structures. It has also been found that heat-degraded polyvinyl chloride shows a strong absorption peak at 2730 A., indicating the presence of carbonyl groups. The absorption curve between 2500 and 3500 A. is very similar to those of oxidized α-eleostearic acid or crotonylidene acetone Me·CH:CH·CH:COMe and suggests further the presence of a similar keto-olefine structure in all the substances. This view is given

further support by infra-red data. Tail-off into the visible region of the strong absorption at this peak may introduce colour into the polymer.

Heat-stabilizers are generally absorbers for the hydrogen chloride evolved (possibly a catalyst for the decomposition), or are directed to forming Diels–Alder adducts with the polymers, or as with alkyl-tin salts (e.g. dibutyl-tin dilaurate) might give a 'reactive molecular' stabilizer effect. Tests on a few heat-stabilizers indicate that the acid-absorbing basic lead salt type of stabilizer is the most effective in preserving good colour.

Light degradation of polyvinyl chloride is suggested as beginning by light absorption at polyene systems already present in the hot-processed polymer. The absorbed energy initiates oxidation, degradation, and further development of colour. Brittleness also develops and is attributed to cross-linking between polymer chains. Heat degradation of plasticizers may also assist light degradation of the polymer. Stabilization against light degradation includes incorporation of screening agents ranging from complete opacifiers such as carbon black to ultra-violet absorbing substances such as phenyl or lead salicylate. Other methods are to eliminate polyenes by 'reactive molecules' or to incorporate anti-oxidants which would reduce carbonyl formation and inhibit free-radical transmission of the light energy.

Among proposed heat-stabilizers for polyvinyl chloride are: salts of *ortho*-sulphobenzimide[77]; tetra-α-thienyl tin[78]; zirconium oxide[79]; alkali stannates.[80] New light-stabilizers for this polymer include: monoximes of 1 : 2-diketones or ketoaldehydes[81]; tri-*p*-chlorophenyl stibine[82]; 2-hydroxy-5-chlorobenzophenone-2′-carboxylic acid.[83]

Fabricated unplasticized polyvinyl chloride possesses a number of good features which make it an attractive constructional material. Production of tubes and rod from the straight polymer calls for special techniques, principally because the practical working temperature is close to the decomposition temperature of the polyvinyl chloride. A. Burness, J. R. Cann and P. Ions[84] describe work on the extrusion of unplasticized vinyl chloride by hydraulic ram, and by single- and double-screw extrusion machines. The polymer should be of lower molecular weight than that normally used in plasticized composition; this change lowers the working temperature and makes possible continuous operation of the extrusion process without decomposition troubles. Heat stabilizer (e.g. diphenylthiourea) must be incorporated in the polymer. Calcium stearate is a satisfactory lubricant. Use of pre-rolled chip composition for feed to a single-screw extruder gives easier control of the extrusion. It is fundamental for successful extrusion of unplasticized polyvinyl chloride to avoid overheating, to streamline all flow surfaces so as to avoid pockets of static polymer (which decomposes), and to look to general cleanliness of equipment. A separate part of the article describes the machines used, including Colombo, Eckert and Ziegler, Mapré 'Trudex' and La Boudineuse Universelle double-screw extruders.

The processing of plasticized or unplasticized polyvinyl chloride to foamed masses is described by Mlle. G. van Gaver.[85] Materials which evolve gas by their decomposition at elevated temperature are mixed

with polymer and plasticizer, and the whole is heated in a gas-tight mould to the temperature necessary to decompose the foaming agent and plasticize the polymer. Reduction of pressure after some cooling leads to expansion of the gas and foaming of the plastic. Sodium bicarbonate gives sponges (interconnecting cells); discrete cells are produced by the use of azo-compounds such as azo-di-*iso*butyronitrile. The foamed plastics have bulk densities in the range 0·05 to 0·16.

The heat-sealing and sewing of plasticized polyvinyl chloride films have been studied by H. Beck.[86] Methods of carrying out these operations have been extensively examined. Heat-sealing is the proper way of uniting polyvinyl chloride films, and special apparatus has been developed to give heat-seals approaching the base material in strength. Silver swaging tools give considerable increase in speed of sealing but this is always lower than when sewing is used. Sewed seams readily tear through because of notching where the needle perforates, and they can only be used where no great mechanical demands are made on the film.

Rheological study[87] of plasticized polyvinyl chloride leads to the conclusion that there is a 3-dimensional network system present, with partial crystallization. The rubbery nature of thermo-plasticized polyvinyl chloride makes necessary[88] special techniques for embossing designs on sheet made from this polymer. It is necessary to heat the material to 160° C. and pass it immediately into the embossing roll, which is water-cooled to 'freeze-in' the embossed pattern before the material passes out. Special backing rolls based on elastic material are employed to counter the embossing rolls; the ordinary wool-paper rolls are unsuitable. Close control of temperature and speed of operation are necessary to strike the balance between too low embossing temperature which does not give a pattern, and too high, which causes burning. Colours can be embossed into the material from pigment applied to the peaks of the engraved surface of the embossing roll.

In a review devoted to trends in the coating of fabrics with polyvinyl chloride and its copolymers,[89] the relative technical attractiveness of 'plastisols,' i.e. polymer–plasticizer pastes, and 'organosols,' which are plastisols with addition of small amounts of cheap, volatile diluent, is emphasized in comparison with the older solution techniques, which require expensive solvent-recovery plant. Plastic coatings tend to become thicker, and base fabric thinner. Types of oven employed for drying and fusing the new coatings are discussed. Glass fibre-enclosed radiant heaters are very promising for this treatment, enabling heating tunnels to be much shorter than tunnels using hot gas heating. To obtain polyvinyl chloride–plasticizer pastes[90] giving gels of the required mechanical properties, it is desirable to have polymer particles of small average size and wide size-distribution. This gives good packing of polymer and minimum requirements of plasticizer. The thixotropic properties in the paste desirable for spreading are in part obtained by having a soft envelope of plasticized polymer on the particles. With pastes, heavy coatings on fabric can be obtained with only 2 or 3 passes. In the use of paste for hollow-casting and hot-dipping, steel, aluminium and chromium-plated moulds and formers are satisfactory, but zinc, zinc alloys (and zinc salts) cause decomposition of the polyvinyl chloride.

Polyvinyl esters, alcohol and ethers

An approximately linear relationship[91] between $(\eta)^{1\cdot 4}$ and tack temperature holds for polyvinyl acetates. The adhesion of polyvinyl acetate to cellulose and aluminium is independent of molecular weight above a certain value, below which failure is due to insufficient cohesion within the polymer, owing presumably to chain slip.

Reagents which attack 1 : 2-diol structure to break the carbon linkage[92] (periodic acid, sodium periodate, lead tetra-acetate) have been shown to cause a rapid fall in the intrinsic viscosity of polyvinyl alcohol solutions. The extent of the effect is about the same with each reagent, and after the initial rapid fall the viscosity stays virtually steady. The degree of degradation of the polyvinyl alcohol thus produced is limited, the final product having a molecular weight between 3700 and 6500. The extent of degradation seems to depend solely on the temperature of polymerization of the vinyl acetate. The existence of the 1 : 2-diol structures is attributed to occasional head-to-head additions during polymerization of the vinyl acetate (1·23% at 20° c.; 1·95% at 110° c.). The abnormal addition reaction has an activation energy 1250 cal. higher than for the normal addition, and a steric factor about 1/10 that of the normal. Polyvinyl alcohol may be prepared from and reconverted to polyvinyl acetate without degradation.[93]

Russian and American polyvinyl alcohol polarizing filters have been tested[94] in the range 2500–15,000 A. by spectrophotometer. The filters give 100% polarization in the range 2500–8000 A. the effect falling to zero between 8000 and 9000 A. and being absent up to 13,000 A. Approximately 30% of incident white light is transmitted; in the visible range they are neutral.

C. E. Schildknecht, S. T. Gross and A. O. Zoss,[95] after reviewing the subject of isomerism in polymers (branching, monomer addition order, and especially stereoisomerism) and its effect on properties, discuss the apparent stereoisomerism in polyvinyl methyl and *iso*butyl ethers. Two forms of *iso*butyl ether polymers are produced by low-temperature polymerization with ionic catalyst. Rapid polymerization (BF_3 gas catalyst) produces a rubber-like polymer and slower polyphase growth of polymer on BF_3 etherate, a crystalline type, both species being apparent entities with no tendency to pass into the other form; similar remarks apply to the methyl ether polymers. The possibilities are discussed of the existence of these different types being due to differences in sequence of D- and L-polymer units, and to kinks, bends or spirals stabilized by restricted rotation of the C–C bonds in the main chain.

Fluorine-containing polymers

W. C. Fergusson[96] has reviewed the history, properties and processing techniques of polytetrafluoroethylene. Polymerization of the monomer over aqueous persulphate gives a white granular solid. Chemically, the polymer is distinguished by extreme inertness; only alkali metals and elementary fluorine attack it, at high temperature. Although no solvent has yet been found the polymer is highly crystalline, and its structure is considered to be linear, composed of $-CF_2{\cdot}CF_2-$units without, as far as can be ascertained, any branching. The molecular weight of the polymer is

unknown. The high softening point and high melt-viscosity are considered to follow from the molecular structure rather than from very high molecular weight. Restricted rotation of carbon atoms in the polymer chain is thought to be due probably to electrostatic repulsion of fluorine atoms, and to their size; as a result the activation energies of flow are very high, sufficient to inhibit such flow below the decomposition temperature of the polymer. The fabricated polymer has tensile strength 2000 lb./sq. in. with 50–400% elongation, is tough and flexible in thin sheets, and remains so at very low temperatures. Cold drawing improves the mechanical properties; the tensile strength of drawn thin films can reach 1500 lb./sq. in., and reasonably good mechanical properties are shown up to 200–250° c. The electrical properties are excellent, the low power factor (0·0002) being retained over a wide frequency and temperature range. Volume- and surface-resistivity are high, and the polymer shows non-tracking properties because of the absence of carbonization by the arc. Because of the non-fusibility of the polymer fabricating methods depend essentially on sintering procedures. Various techniques are described.

Polytrifluorochloroethylene, first prepared in Germany in the middle thirties, is now being produced commercially[97] on a limited scale. Although it possesses to a considerable degree the inertness and high-temperature stability of polytetrafluoroethylene, it can be fabricated by the techniques used for normal thermoplastics, but at comparatively high temperatures (290–315° c.), and it can thus be compression-, transfer- or injection-moulded, or extruded. The tensile strength is 9400 lb./sq. in. at 32° c., with 127% elongation, and the material is tough and flexible so that it can be punched, drilled or machined to close limits. Its crystallinity results in the moulded polymer becoming translucent on slow cooling, but sections of moderate thickness can be shock-cooled to give transparent products, which are more flexible although less hard than the slow-cooled material. The material does not absorb water and is reported to be unchanged on outdoor exposure. It exhibits low cold-flow. The mechanical properties are stated to be satisfactory over the range − 195°c. to + 200° c. These properties make the material attractive for a number of special uses.

Acrylic polymers

An indirect method of oxidizing acrolein to acrylic acid consists in adding acetic acid across the double bond in the acrolein, oxidizing the product with molecular oxygen and a catalyst to acetoxypropionic acid and pyrolysing the latter to yield acrylic and acetic acids.[98] High-temperature (250–400° c.) vapour-phase chlorination of acrolein[99] or methacrolein with an excess of aldehyde over the stoichiometric equimolar proportions of aldehyde and chlorine leads to formation of acrylyl and methacrylyl chlorides by substitution of the aldehyde hydrogen. D. S. Davis[100] gives a nomograph for ascertaining the boiling point, between 1 and 1000 mm. pressure, of a series of *n*-alkyl acrylates and methacrylates between methyl and hexadecyl.

H. S. Kaufman *et al.*[101] show that the crystallinity of polymers of acrylic esters with long-chain normal alcohol alkyl radicals is due to

crystallization of the n-alkyl side chains. At a fairly sharp melting point this ordered structure breaks down, the waxy polymer passing into a rubber. It is thought from X-ray spacing data that there is a periodicity in the side-chain packing every six monomer units. W. C. Mast and C. H. Fisher[102] have copolymerized ethyl acrylate with 28 materials containing diene or polyolefine bondings in an attempt to obtain vulcanizable rubbery substances. The copolymers were insoluble in organic solvents, pointing to some cross-linking having occurred during copolymerization. The most practical rubbery vulcanizate was obtained from an ethyl acrylate–acrylonitrile–vinyl ether copolymer. The polymers of alkoxyalkyl acrylates and methacrylates,[103] $R(O{\cdot}CH_2{\cdot}CH_2)_n{\cdot}O{\cdot}CO{\cdot}CHR:CH_2$, are soft, rubbery and soluble when made in the usual way; but on stoving in presence of air or oxygen, especially in presence of cobalt or similar 'driers,' they pass into glossy, hard, flexible, thermoset materials, the process apparently involving absorption of oxygen.

The properties of a number of polymethacrylic esters of higher alcohols have been examined. Properties are affected by branching in the alcohol alkyl group, and the possibility is examined of induction by methyl groups in the alcohol alkyls exerting an influence on properties of the polymer.[104] Trichloroethyl methacrylate polymerizes to a clear resin which is non-combustible; it has been proposed for glazing purposes.[105] The techniques involved in the production and fabrication of cast polymethyl methacrylate sheet are discussed in some detail by C. T. Kautter.[106] Difficulties encountered in the casting process due to the polymerization heat and the shrinkage on polymerization are gone into.

The application of methacrylate sheet in the production of lighting fittings is described by W. E. Harper.[107] The material is of especial interest in conjunction with fluorescent lamps where the low heat dissipation makes demoulding of the plastic fitting very unlikely. Opal material is especially useful for reflectors for these lamps. Street and mine lighting, with fluorescent tubes in methacrylate fittings, are discussed. Experience has shown that fears of surface abrasion by dust and cleaning operations are unfounded. Clear refractor plates for sodium- or mercury-vapour street lamps are hot moulded from methacrylate sheet with high accuracy. Methyl methacrylate–maleic or –methacrylic acid copolymers in the ratio 85 : 15 give clear cast sheets.[108] Immersed in potassium hydroxide solution, the surface carboxyl groups form salts; transference of the alkali-treated sheet of copolymer to a solution of a metal salt results in the carboxyls in the surface of the copolymer being converted to metal salts. In a number of cases, such clear metal-containing sheets show a higher abrasion resistance than the initial copolymer. Stannous and uranyl salts gave the best abrasion resistance for the methacrylic acid copolymer, and strontium and uranyl salts for the maleic acid copolymer.

The heating of water-suspended polymethyl methacrylate particles with small amounts of aliphatic mercaptan[109] (C_1–C_{18}) to a temperature 30° C. below the flow temperature of the polymer gives a product of increased heat (depolymerization) resistance, presumably by inhibitor effect on depolymerization runs in the macromolecules. The injection moulding of methacrylate lenses[110] for the finder system of reflex cameras,

small viewer lenses and watch glasses presents a number of technical problems in obtaining lenses of satisfactory accuracy. Large gates, slow injection, very highly polished moulds which do not require chromium plating are features of successful practice. Increase of surface hardness of the moulded lenses is the objective of much current research. Moulded acrylic lenses are making rapid headway as a preferred material in U.S.A. for production of automobile lenses,[111] in competition with glass; the acrylic products are claimed to have higher brilliancy, greater colour stability, and to be practically unbreakable; they can be made in special shapes impracticable in glass, are dimensionally stable and are readily fitted in position in their components; moulding techniques are described. In a comparison of methacrylate polymer dental resins, W. Johnson and E. Matthews[112] shows that a copolymer of ethyl and methyl methacrylate shows similar Brinell hardness and tensile strength to straight polymethyl methacrylate, while possessing a definitely superior flexural fatigue strength.

Acrylonitrile

The synthesis of acrylonitrile from acetylene and hydrogen cyanide using Nieuwland's cuprous chloride catalysts is discussed by P. Kurtz[113]; this new synthesis has been thoroughly studied and optimum conditions obtained; yields are claimed to be 80% on acetylene and 85% on hydrogen cyanide.

According to H. Rein[114] polyacrylonitrile fibres were first developed in Germany. The failure of conventional methods to deal with the spinning problem led to the discovery of the solvent properties for the polymer of cyclic ethers, lactones and similar ring-structured materials; later, H. Rein discovered the solvent properties for polyacrylonitrile of dimethylformamide: this is the solvent used in manufacturing practice to-day. The properties of polyacrylonitrile fibre are given, in comparison with other synthetic and natural fibres. Its warm feel is nearest to natural silk of the synthetic fibres, and it has high elasticity, springiness and recovery. The softening point is over 200° c., and combustibility is like that of cellulose fibre. The resistance to ferments is second only to chlorinated polyvinyl chloride, and resistance to insects is similar to that of nylon. Resistance to degradation of mechanical properties on outdoor exposure is quite outstanding. Fabrics of polyacrylonitrile fibre are easily washed; oil and grease adhere only superficially and are very easily removed. The fibres may be dyed by a series of acetate dyes, more strongly in presence of swelling agents. Applications for polyacrylonitrile fabrics are reviewed. Several American assessments of du Pont's polyacrylonitrile fibre ('Orlon') have appeared.[115] Solvents useful in du Pont's experience[116] for spinning polyacrylonitrile include dimethylformamide, dimethylmethoxyacetamide, tetramethylene sulphone and *m*- and *p*-nitrophenols.

The properties of acrylonitrile–vinyl chloride copolymer ('Vinyon N,' 'Dynel') are discussed, mainly from the point of view of textile applications.[117]

Polyethenoid polymers

As the result of the influence of a number of factors, it is considered[118] that 'reinforced polyesters' (previously called 'low-pressure laminates') are moving into fields of greater application. The use of matched metal dies for pressing the glass fibre–polyester lay-ups during curing gives better finish on both sides of the cured product, and, with cut-off rings on the moulds, reduction of handling and finishing costs. The moulds are more expensive than the earlier tools used for the purpose, but less expensive than injection or compression moulding dies. Such dies are used for trays, tubs, chairs, radomes etc. The polyesters themselves have been improved and cheapened, and the highly important cost of the glass fibre filler has come down; methods of using the cheapest, random-oriented glass fibre have been developed. Various ways of hiding the glass mat in the finished article, by appropriate finishing techniques, have come into use. In a discussion of the future of reinforced polyesters and continuous laminates, the present uncertainty for the investor is brought out.

H. W. De Vore[119] has reviewed technical development of the fast-moulding alkyd thermosetting powders described by M. H. Bigelow.[120] The moulded plastic possesses outstandingly high arc-resistance and non-tracking properties, high dimensional stability, low coefficient of expansion, low water-absorption and high heat-resistance; the loss factor is sufficiently small to enable the plastic to be used in radar and television components. The review summarizes results obtained in trials by the electrical industry.

The allyl ether of starch, first made in 1923 by Tomecko and Adams, was developed in 1944 by the U.S. Department of Agriculture, and has now been put on a pilot-plant manufacturing scale by General Mills Research Laboratories. The technical product contains approximately 1·7 allyl groups per glucose unit, and is prepared from allyl chloride and starch; these readily available starting materials make the material economically of interest. The properties are described by M. H. Baker.[121] Allyl starch is soluble in a variety of organic solvents; films deposited from solutions dry readily in presence of cobalt, or better by baking at 100–125° c. without driers. The cured films are hard, with high gloss, solvent-, acid- and water-resistant; the material appears to be non-toxic. Shrinkage of allyl starch on curing leads to strains in the film with subsequent checking or crazing, overcome by use of 10–20% of plasticizer. The polymer has the property of making paper transparent when coated on it.

Quaternary ammonium halides containing 2–4 unsaturated radicals per molecule have been prepared and polymerized by G. B. Butler and R. L. Bunch.[122] Inhibition of polymerization, frequently observed with amines, did not occur with these salts. Polymerization was carried out on melts; the melting points were lowered by admixture of the halides with one another or by adding very small amounts of water or formamide, which lower the fusion temperatures greatly; peroxide catalyst was used. Solutions of the halides in water could not be polymerized. Cross-linking of the polymer chains resulted in the ammonium cations being

contained in an insoluble network. These resins show powerful ion-exchange properties.

Miscellaneous polymers

R. M. Fuoss. G. I. Cathers and W. S. Albrink[123] have examined the electrical properties of the reaction product of styrene–4-vinylpyridine copolymer with *n*-butyl bromide: this is a copolymer in which the *tetra*-alkylammonium cations are immobilized in the macromolecules. Solutions of the copolymer in nitromethane–dioxan mixtures show a tendency towards a high degree of ionic association of the copolymers, controlled by the amount of ammonium component in the copolymer and by the dielectric constant of the solvent. The conductance of the solutions indicates that under the influence of electrostatic forces a fraction of the anions accompanies the large poly-cation and does not contribute to the conductance. Films of the copolymer placed as membranes between electrolytes can be represented by an electrical conductance in parallel with a pure a.c. impedance whose real and imaginary components resemble in their relationship to one another that found by Cole and co-workers for a variety of biological membranes.

H. G. Cassidy[124] has demonstrated that polyvinylhydroquinone is an electron-exchange resin with analogies to proton-exchange resins. Oxidation of the colourless polymer to yellow polyvinylquinone by bromine or ceric sulphate has been carried out; the polyquinone is reduced catalytically by hydrogen back to the hydroquinone, which can be oxidized back to quinone along the same potential-conversion curve. Formation of pink colour in the middle stages of the oxidation is probably associated with formation of semi-quinone. Preparation and polymerization of vinylhydroquinone are described.

A detailed study has been made by J. C. Berington and R. G. W. Norrish[125] of the polymerization reaction of acetaldehyde yielding macromolecular products. Water, acetone and ethyl alcohol show an inhibiting action on the polymerization; acetic acid increased the yield of polymer while reducing the molecular weight and stability. The weight of polymer produced was a function of rate of distillation of acetaldehyde into the cooled receiver and of the amount of monomer used. Solidification is essential for polymerization. The polymer, which is considered to be a methyl-substituted polyoxymethylene, does not require a catalyst for its formation; a suggested polymerization mechanism is given, based on polarization of the acetaldehyde molecule. The number-average molecular weight of a sample of acetaldehyde polymer,[126] freed from volatile decomposition products, was $5{\cdot}1 \times 10^5$ by osmotic pressure measurement in methyl ethyl ketone.

References

[1] *J. Res. nat. Bur. Stand.*, 1948, **41**, 151
[2] *J. Polymer Sci.*, 1949, **4**, 273
[3] *J. chem. Phys.*, 1948, **16**, 592
[4] *J. Amer. chem. Soc.*, 1949, **70**, 3695
[5] *J. Polymer Sci.*, 1948, **3**, 891
[6] Seebold, J. E., Standard Oil Co. of Indiana, U.S.P. 2,475,643
[7] McSweeney, E. E., Standard Oil Co. of Indiana, U.S.P. 2,475,628

[8] *Ind. Eng. Chem.*, 1949, **41**, 986
[9] Johnson, P. H. and Bibb, R. L., *Ind. Eng. Chem.*, 1949, **41**, 1577
[10] Meyer, A. W., ibid., 1570
[11] Carr, E. L. and Johnson, P. H., ibid., 1588
[12] Mitchell, J. M., Spolsky, R. and Williams, H. L., ibid., 1592
[13] *Bull. Soc. Chim. Belg.*, 1948, **57**, 381
[14] Breitenbach, Richter, *Mh. Chem.*, 1949, **80**, 315
[15] Alexander, C. H., B. F. Goodrich Co., B.P. 609,289
[16] B. F. Goodrich Co., B.P. 627,265
[17] *Nature*, 1949, **163**, 325
[18] *Mem. Serv. Chim. Etat, Paris*, 1945, **32**, 319
[19] Matheson, M. S., Auer, E. E., Bevilacqua E. B. and Hart, E. E., *J. Amer. chem. Soc.*, 1949, **71**, 2610
[20] *Proc. roy. Soc.*, 1949[A], **197**, 356
[21] Ibid., **192**, 309, 329
[22] Ibid., **163**, 511
[23] Matheson, M. S., Auer, E. E., Bevilaoqua, E. B. and Hart, E. E., *J. Amer. chem. Soc.*, 1949, **71**, 497
[24] *Angew. Chem.*, 1949, **61**, 168
[25] Ibid., **60**, 255
[26] *Rubb. Age, Lond.*, 1949, **65**, 545
[27] *Nature*, 1949, **164**, 404
[28] Overberger, C. G., O'Shaughnessy, M. J. and Shalit, H., *J. Amer. chem. Soc.*, 1949, **71**, 2661
[29] *Canad. J. Res.*, 1949, **26B**, 657
[30] *Trans. Faraday Soc.*, 1949, **45**, 425
[31] *J. Amer. chem. Soc.*, 1949, **71**, 1595
[32] Beaman, R. G., ibid., 1948, **70**, 3115
[33] Bachman, G. B., Hass, H. B. and Kahler, E. J., *Ind. Eng. Chem.*, 1949, **41**, 135
[34] Gregg, R. A., Alderman, D. M. and Mayo, F. R., *J. Amer. chem. Soc.*, 1948, **70**, 3740
[35] Küchler, L., *Makromol. Chem.*, 1948, **2**, 176–86
[36] *J. Polymer Sci.*, 1948, **3**, 693
[37] *J. Res. nat. Bur. Stand.*, 1948, **41**, 521
[38] Alfrey, T. junr., *Trans. N.Y. Acad. Sci.*, 1948, **10**, 298
[39] *J. Polymer Sci.*, 1948, **3**, 866
[40] Alfrey, T., junr., Arnold, L. and Overberger, C. G., ibid., 1949, **4**, 539
[41] Siegel, B. M., Johnson, D. H. and Mark H. F., *J. appl. Phys.*, 1949, **19**, 1187
[42] *C.R. Acad. Sci., Paris*, 1948, **227**, 902
[43] Ibid., 1101
[44] *J. Polymer Sci.*, 1948, **3**, 669
[45] *J. appl. Phys.*, 1949, **20**, 540
[46] Stöcklin, F., *Kunststoffe*, 1949, **39**, 228
[47] *Mod. Plastics*, Oct., 1948, **26**, 123
[48] Ibid., Dec., 1948, **26**, 127
[49] *J. Polymer Sci.*, 1948, **3**, 647
[50] *Proc. Amer. Acad.*, 1948, **76**, 71
[51] *Proc. Inst. elec. Engrs.*, 1949, **96**, 37
[52] *J. Polymer Sci.*, 1948, **3**, 652
[53] *Ind. des Plast.*, 1948, **4**, 552
[54] *J. chem. Phys.*, 1949, **17**, 279
[55] Scott, R. L., ibid., 268
[56] High-Polymer Physics Symposium, 1949, 497
[57] *Bull. Soc. Chim. Belg.*, 1948, **57**, 421
[58] *Chem. Engng. News*, 1949, **27**, 2490
[59] *Rev. sci. Instrum.*, 1948, **19**, 331
[60] *Mod. Plastics*, Sept., 1949, **27**, 82
[61] *Proc. Inst. elec. Engrs.*, 1949, Part I, **96**, 44
[62] Parks, G. S. and Mosley, J. R., *J. chem. Phys.*, 1949, **17**, 691
[63] *Acta Crystall.*, 1949, **2**, 85
[64] U.S.P. 2,457,238
[65] *Mod. Plastics*, Dec., 1948, **26**, 119
[66] Morriston Davies, H., *Thorax*, Dec., 1948, **3**, No. 4.
[67] *J. of Plastic and Reconstructive Surgery*, 1948

[68] Jones, J. P., *Chem. Engng. News*, 1949, **27**, 454
[69] Nickels, J. E., Webb, G. A., Heintzman, W. and Corson, B. B., *Ind. Eng. Chem.*, 1949, **41**, 563
[70] Shih-Wei, *J. Phys. Colloid. Chem.*, 1949, **53**, 486
[71] *Ind. Eng. Chem.*, 1949, **41**, 1988
[72] *J. appl. Phys.*, 1949, **20**, 507
[73] U.S.P. 2,473,798
[74] Bueche, A. M., *J. Amer. chem. Soc.*, 1949, **71**, 1452
[75] Norsk Hydro-Elektrisk, B.P. 622,935
[76] Fox, V. W., Hendricks, J. G. and Ratti, H. J., *Ind. Eng. Chem.*, 1949, **41**, 1774
[77] Monsanto Chemical Co., R. H. Schlattman, U.S.P. 2,455,611–4
[78] Idem, Fincke, J. H. and Gluesenkamp, E. W., U.S.P. 2,479,918
[79] Wingfoot Corpn., Cox, F. W. and Wallace, J. M. junr., U.S.P. 2,459,127
[80] Lonzawerke, Swiss Pat. 242,851
[81] Firestone Tire and Rubber Co., Le Claire, C. D., U.S.P. 2,476,829
[82] Monsanto Chemical Co., Park, H. F., U.S.P. 2,456,565
[83] Dow Chemical Co., Havens, C. B., U.S.P. 2,455,674
[84] *Brit. Plastics*, 1949, **21**, 472, 565
[85] *Rev. gén. Caoutch.*, 1949, **26**, 279
[86] *Kunststoffe*, 1949, **39**, 205
[87] Alfrey, T., junr., Wiederhorn, N., Stein, R. and Tobolsky, A., *J. Colloid Sci.*, 1949, **4**, 211
[88] Ploenes, H., *Melliand Textilber*, 1949, **30**, 475
[89] *Mod. Plastics*, Nov., 1949, **27**, 86
[90] Clarkson, D. L. and MacLeod, N. D., *Chem. & Ind.*, **1949**, 304
[91] McLaren, A. D. and Seiler, C. J., *J. Polymer Sci.*, 1949, **4**, 63
[92] Flory, P. J. and Leutner, F. S., ibid., 1948, **3**, 880
[93] Korshak, V. V. and Zamyatina, V. A., *Bull. Acad. Sci., U.R.S.S.* (*Chemistry Class*), 1946, **106**
[94] Godina, D. A., *J. tech. Phys. U.R.S.S.*, 1948, **18**, 1317
[95] *Ind. Eng. Chem.*, 1949, **41**, 1998
[96] *Chem. & Ind.*, **1949**, 586
[97] *Chem. Engng.*, Oct., 1948, **55**, 161; Jan., 1949, **56**, 278
[98] Shell Development Co., Ballard, S. A. and Geyer, B. P., U.S.P. 2,459,677
[99] Bataafsche Petroleum Maatsh., B.P. 626,772
[100] *Chem. Industr.*, 1948, **63**, 844
[101] *J. Amer. chem. Soc.*, 1948, **70**, 3147
[102] *India Rubb. World*, 1949, **119**, 727
[103] Rehberg, C. E., Fisher, C. H., U.S.P. 2,458,888
[104] Crawford, J. W. C., *J. Soc. chem. Ind.*, 1949, **68**, 201
[105] Lonzawerke, Swiss Pat. 245,075, 245,683
[106] *Brit. Plastics*, 1949, **21**, 332, 390
[107] Ibid., 1948, **20**, 583
[108] Seymour, R. B. and Branum, J., junr., *Ind. Eng. Chem.*, 1949, **41**, 1479, 1482
[109] Du Pont, Quinn, J. L., U.S.P. 2,462,895
[110] *Mod. Plastics*, July, 1949, **26**, 85
[111] Ibid., Nov., 1949, **27**, 101
[112] *Brit. dent. J.*, 1949, **86**, 252
[113] *Angew Chem.*, 1949, **61**, 34; CIOS XXIII–25
[114] Ibid., 241
[115] *Text. World*, Sept., 1949, 102a; *Rayon synth. Text.*, Feb., 1949, **30**, 79; Mar., 1949, **30**, 67
[116] *Chem. Industr.*, 1949, **64**, 36
[117] *Rayon synth. Text.*, Jan., 1949, **30**, 65; Feb., 1949, **30**, 81
[118] *Mod. Plastics*, Oct., 1949, **27**, 69
[119] Ibid., Nov., 1949, **27**, 81
[120] Ibid., Oct., 1948, **26**, 85
[121] *Mod. Packaging*, May, 1949, **22**, 131
[122] *J. Amer. chem. Soc.*, 1949, **71**, 3120
[123] *J. Polymer Sci.*, 1949, **4**, 97; *J. gen. Physiol.*, 1949, **32**, 454
[124] *J. Amer. chem. Soc.*, 1949, **71**, 402, 407
[125] *Proc. roy. Soc.*, 1949[A], **196**, 363
[126] Muhtana, M. S. and Mark, H., *J. Polymer Sci.*, 1949, **4**, 91

POLYCONDENSATION PRODUCTS (A. A. K. Whitehouse, M.A., F.R.I.C.)

Among the most important developments reviewed below are the work on phenolic resin structures and the reactions of intermediates, the reports of war-time studies in Japan of phenol–furfural resins, and in Germany of xylene–formaldehyde resins, some American polarographic studies of urea–formaldehyde condensation, and the continued development of polyethylene terephthalate in Britain.

The amount of space devoted to different materials in this review may tend to give a wrong impression of the relative importance of the various plastics. New materials which are being actively developed tend to get more space than their present importance warrants, whereas a number of general subjects are treated for convenience under phenoplastics and this increases the size of this section. Actual production figures for the two major types of polycondensation product in Britain were, in thousands of tons, as follows[1] :

	1945	1946	1947	1948
Phenol–formaldehyde resins ..	17·1	22·3	22·7	25·6
Urea–formaldehyde resins ..	7·9	11·7	15·5	16·4
Phenolic moulding materials ..	17·5	25·2	24·7	26·8
Urea moulding materials ..	4·0	6·5	7·9	8·9

Phenoplastics

Theory and structure

Some of the continental workers whose war-time papers on the chemistry of the hardening of phenolic resols were reviewed in Annual Reports two years ago have now renewed their studies in earnest. In particular Zinke and Ziegler and their co-workers at the University of Graz in Austria have published nearly 20 papers during the past two years on the organic chemistry of phenolic resin intermediates. Hultzsch in Germany is also continuing his studies on the same subject.

Phenol alcohols have received particular attention. Their direct preparation from phenols and paraform has been described,[2] and Ziegler has published a whole series of papers[3] on some of their chemical reactions. Three of these papers [3b,d,h] relate to the reaction of phenol alcohols with diazonium compounds : formaldehyde is split off and the diazo-compound couples in its place with the phenol in the *ortho-* or preferably in the *para*-position.

The reaction takes place immediately in the presence of 10% aqueous alkali at room temperature or at 0° c., and the yields are usually 70–90%. When two methylol groups are present one or both may be replaced according to conditions, although *o*-cresol dialcohol and guaiacol dialcohol both couple in the *para*-position splitting off formaldehyde, and the methylol groups do not react.[3d] *p*-Cresol monoalcohol does not couple in the unoccupied *ortho*-position, but only by splitting off formaldehyde from the occupied position—in 70% yield. Saligenin on the other hand couples in the free *para*-position without splitting off formaldehyde.[3h]

Coupling in the *para*-position seems always to be preferred where it is possible.

Ziegler and Zigeuner[4] have also found that condensation products of the dihydroxydiphenylmethane type may be cleaved with diazonium compounds into their original ketones or aldehydes, and the phenols coupled with the diazo-compound, e.g. diphenylolpropane and related compounds are cleaved as follows:

$$OH\cdot C_6H_4\cdot CRR'\cdot C_6H_4\cdot OH + 2PhN_2 + 2NaOH \rightarrow 2Ph\cdot N:N\cdot C_6H_4\cdot OH + R\cdot CO\cdot R' + 2NaCl + H_2O$$

This reaction also takes place readily at room temperature in alkaline solution. Cleavage occurs in the *para*-position even when unreacted *ortho*-positions are available, and the reaction still occurs when one of the two hydroxyl groups is masked by benzdioxan formation. The occurrence of this reaction clearly shows that it is not permissible on the ground of easy coupling to deduce the presence of free positions on the nucleus. The authors suggest that the reaction should be of value for determining the constitution of phenolic resins and of lignin.

Another valuable reaction of phenol alcohols is that leading to the introduction of thiocyanate groups by direct treatment with potassium thiocyanate and an acid at room temperature.[3g] This is valuable because the methyl thiocyanate groups can then be converted to chloromethyl groups by passing hydrogen chloride gas into a benzene solution of the thiocyanate methyl derivative; this provides a convenient method of obtaining the reactive chloromethyl derivatives. By choosing suitable proportions one or both of the methylol groups of a dialcohol such as *p*-cresol dialcohol may be converted into the thiocyanate methyl and chloromethyl groups.

The chloromethyl derivatives of phenols, or *pseudo*halogenides as the Austrian workers describe them, are highly reactive substances valuable for synthetic work. With phenols they give dihydroxydiphenylmethane and related multi-ring compounds [3a,f] and with phenol alcohols good yields, e.g. 80%, of ether-linked polyphenols may be prepared.[3e] The chloromethyl derivatives are also formed by the action of hydrochloric acid on phenol alcohols and are stated by Ziegler[3a,i,j] to be undoubted intermediates in hydrochloric acid-catalysed novolak formation. It is interesting to note that in the synthesis of multi-ring methylene-bridged intermediates with these compounds reaction takes place preferentially in the *para*-position—almost exclusively in many cases.[3f]

Several reactions of phenol alcohols in which the phenolic hydroxyls remain unchanged have been discussed. The reverse phenomenon of reaction at the phenolic hydroxyl without affecting the methylol group may occur. Warming a resol in alkaline solution with ethylene oxide causes etherification of the phenolic hydroxyl groups of the phenol alcohol molecules.[5]

$$C_6H_4(OH)\cdot CH_2OH + \overset{O}{CH_2\text{—}CH_2} \rightarrow C_6H_4(O\cdot CH_2\cdot CH_2OH)\cdot CH_2OH$$

Some American work on phenol alcohols has also been published recently. Ruderman [6a] has given details of the preparation of a number

of alkylphenol dialcohols, and of the condensation of thiols with phenol alcohols in the presence of Friedel–Crafts' catalysts to give methylene thioethers of phenol.[6b] This reaction if carried out with phenol di- or tri-alcohols and polythiols should yield polymers.

A preliminary note about a paper by Sprengling and Freeman[7] shows that they have estimated the proportions of methylol derivatives formed by the alkaline reaction of one mole of phenol with 1·4 moles of formaldehyde as follows: unreacted phenol 5–10%; saligenin 10–15%; *p*-methylolphenol 35–40%; 2:4-dimethylolphenol 30–35%; 2:6-dimethylolphenol nil; trimethylolphenol 4–8%.

Sprung and Gladstone[8] have made an important contribution to the kinetics of resinification by a study of the condensation of saligenin with itself and with phenol and resorcinol. *Without* catalyst, yields of over 80% of 2 : 2′-dihydroxydibenzyl ether were obtained from saligenin with or without solvent by a second order reaction. This ether is quite stable, being unaffected by boiling aqueous alkali, and it does not therefore appear to be an intermediate in the resinification of saligenin. In confirmation of this it was found that its presence retarded the resinification of saligenin by alkaline catalysts at 100° C. This alkaline resinification of saligenin is a first order reaction, whereas the reaction of saligenin with phenol or resorcinol is second order both in the presence or absence of base or diluent. The method of analysis used for this work was bromination under carefully specified conditions such that complete bromination at unsubstituted *ortho*- and *para*-positions and quantitive elimination of *ortho*- and *para*-methylol groups occurred without over-bromination.

The ammonia-catalysed phenol–formaldehyde reaction has been followed by Finn and Rogers[9] by measuring the temperatures at which samples from the reaction mixture just cloud after various reaction times. These temperatures can be quickly measured to within 0·2° C., and the method is useful for empirical studies of the effects of temperature, and of reactant and catalyst concentration on the progress of reaction. The direct effects of reagent concentration on cloud temperatures are eliminated by bringing the mixture to a standard concentration before testing. The ammonia-catalysed reaction has also been studied by Hultzsch[12c] who finds that di- and tri-methylamine bridges are formed between phenolic nuclei.

Müller and Müller[10b] have used their method of fractional precipitation with acids,[10a] which was described in last year's Report, for following the alkali-catalysed condensation of different phenols with formaldehyde. They define as the 'resitol point' the sharply defined point, some while after the cloud point, when the resin gels. By measuring the 'resitol point' for different phenols they find their relative reaction velocities to be as follows: 1 : 3 : 5-xylenol : *m*-cresol : phenol : *p*-cresol : *o*-cresol as 8·5 : 3·4 : 1·0 : 0·6 : 0·4. Apart from *o*-cresol, the 'resitol point' occurs when about two-thirds of the resin is in the infusible state.

Zinke and co-workers have continued their series of papers on the hardening of phenolic resins.[11] Two of these[11a,d] are concerned with hardening by means of hexamethylenetetramine. Resins hardened with this reagent at moderate temperatures contain nitrogen, probably in the

form of polybenzylamine chains. With more phenol and higher temperatures this nitrogen is split off as ammonia or amines leaving nitrogen-free resins.[11a] When 2 : 4- and 2 : 6-xylenol are heated with hexamethylenetetramine they behave in a similar manner giving dibenzylamine derivatives at temperatures below 140° c., losing ammonia at 160° c. and decomposing further at higher temperatures.[11d]

The hardening of *p-tert.*-butylphenol dialcohol at 125, 140 and 155° c. gives homologous polymers with wholly ether-linked chains as shown by hydrobromic acid cleavage.[11b,c] The cryoscopic molecular weights are proportional to the intrinsic viscosities. At 155° c. the molecular weight is 1423, but heating in the 170–200° c. range reduces both the molecular weight and the hydrobromic acid absorption owing to chain breaking, and some water, formaldehyde and phenol aldehydes are split off. At 215–230° c. the average molecular weight increases again and the authors suggest that quinone methide formation occurs. From *p-tert.*-butylphenol resols heated with alkali, Zinke claims[11f] to have isolated a cyclic 4-nuclear methylene-bridged compound. Parallel work[11e] on *o*-cresol dialcohol shows that this gives homologous polymers up to 160° c.

Hultzsch's recent papers[12] on phenol–formaldehyde resins are mainly comprehensive reviews of earlier work and theoretical analyses of possible reactions. Particular attention is given to the formation of quinone-methides and cyclic quinol ethers (dimeric *o*-quinone methides). The importance of hydrogen bonding in phenol alcohols and other intermediates is emphasized.[12d,e]

Raw materials

Phenol is now synthesized from benzene on a large scale predominantly for the synthetic resin industry which accounts for 60% of U.S.A. production.[13] Of this synthetic phenol 48% is made through chlorobenzene from benzene with either chlorine, or with hydrogen chloride and air reacting in the vapour phase by the Raschig process, and 42% is made by the benzene sulphonation process.[13]

Several recent patents[14] have described methods of direct air oxidation of benzene to phenol in the presence of catalysts such as iodine or cracked gasoline and giving yields of 30–60%. It has been reported[15] from the Socony Vacuum Oil Company's laboratories that non-catalytic vapour-phase oxidation with air will produce significant amounts of phenol if crude benzole is used, owing to the promoting action of certain impurities.

Cresols have up to the present been obtained from coal tar distillation, but an American plant is now under construction for the synthesis of over 1000 tons per annum from toluene.[16] The toluene is passed into sulphuric acid containing a boron catalyst, giving a toluene–boron complex which on subsequent hydrolysis with boiling water gives a mixture of cresols with the *para*-compound predominating.

Recently patented methods for separating and recovering phenols include treatment with alkylating agents or formaldehyde when a more reactive phenol will be selectively removed,[17] and for separating *m*- and *p*-cresol, fractional distillation of the crystalline addition compound

formed at -5 to $-15°$ C. with 2 : 6-dimethylpyridine[18]; this method will convert commercial 55–60% *m*-cresol into an 80% *m*-cresol mixture.

Formaldehyde production capacity in the U.S.A. now amounts to about 400,000 tons per annum of 37% (wt.) formalin.[19] Production is by partial oxidation with air of methanol at 600° C. over a silver catalyst, but lower-boiling petroleum gases may be used in place of methanol.[19,20] Although at present of only academic interest, it may be recorded that Indian workers[21] have prepared formaldehyde directly from carbon monoxide and hydrogen under the silent electric discharge, and methanol has been made directly from carbon dioxide by reduction with lithium aluminium hydride.[22]

Manufacture and processing

A variation of the usual procedure for making moulding resins with either acid or alkaline catalysts has been reported by Pritchett and Barnett.[23] They carry out the initial condensation with an alkaline catalyst to ensure rapid reaction, and then acidify and dehydrate when all the formaldehyde has combined. The molar formaldehyde to phenol ratio must not exceed 0·9 at acidification; if more formaldehyde was initially used, phenol must be added after the alkaline reaction to correct the ratio.

The three isomeric dihydroxydiphenylmethanes condense with formaldehyde at different rates. The 2 : 2′-isomer has been prepared from xanthone[24] and shown to be the most reactive. Further, the use of the oxides of zinc, magnesium or aluminium as catalysts in phenol–formaldehyde condensations favours the formation of this isomer and therefore gives fast-curing resins and moulding materials.[25]

Another catalyst choice is that of ethylenediamine for obtaining resins of exceptionally slight odour.[26] Again for water-soluble resins alkaline condensation with excess formaldehyde may be followed by the addition of resorcinol and inter-reaction at 80–90° C.[27]; for oil-soluble resins of high melting point and low volatility the use of a phenolsulphonic acid for catalysing the condensation of suitable substituted phenols with formaldehyde has been recommended.[28]

Several improvements in the moulding of phenoplastics have recently been described. High-frequency preheating may be carried out while preforms are actually being compressed.[29] With high-frequency heating such variables as moisture content, electrode spacing, height and density of preform and handling and transfer time must be controlled with care.[30] Some improvements in the techniques of transfer- and injection-moulding have been made, in particular a machine which preheats single shots of material by high-frequency current to just below curing temperature, discharges into the injection cylinder at the same temperature and then injects into the mould through a superheated tapered sprue bush.[31]

Testing

The Le Rolland–Sorin elasticimeter provides a useful method of measuring the modulus of elasticity of plastics.[32] A cylindrical test-piece is clamped rigidly at its upper end in a vertical position. The lower end of the test-piece is clamped to a horizontal bar which supports

two identical pendulums at its ends. One pendulum is swung; the amplitude of its swings decreases as those of the other pendulum increase, and vice versa. The time of transfer of momentum from one pendulum to the other is inversely proportional to the elastic modulus of the test piece.

Some studies of the effect of temperature on the flexural strength of laminates have shown that there is a fall in strength with temperature throughout the range $-50°$ to 200°c.[33] Long-period exposure to tempera. tures in the range 25–175°c. for 6 and 12 months indicates that exposure at 65° c. produces a general improvement in strength. With coarse-weave cotton and kraft paper fillers, deterioration occurs at 85° c. and above, but with asbestos or fibre glass fillers deterioration starts only at 135° c.

Bernhardt[34] has made a theoretical analysis of scratch resistance and concludes that it should be expressed by the tangential force required to propagate the scratch along the surface per unit cross-sectional area of scratch. Scratch resistance is independent of depth of scratch or loading but increases with speed of scratch. These considerations and the results obtained with an apparatus designed to measure scratch-resistance apply to scratching by air-blown grit but not to wiping a dirty surface.

Barwell and Pepper[35] have studied the swelling of reinforced plastics in the presence of water. The equilibrium moisture content of phenolic resins is proportional to the relative humidity, but depends markedly on the nature of the phenol and of the catalyst used during condensation and on the degree of cure of the resin. The dimensional changes of laminated plastics as a result of water absorption are greatly influenced by the geometry of the reinforcement and the way it is arranged in the laminate. The hygroscopicity of cellulose fillers is reduced by the resin. Bowman, Fitzgerald and Jensen[36] have emphasized the distinction between rate of penetration and saturation limit. They recommend greater control of the history of specimens or more extended conditioning before water absorption measurements.

Some interesting work on the flow properties of phenolic resins has been carried out by Dienes.[37] He studied novolaks in the range 50–100° c. giving viscosities of 10^3–10^9 poises. These were measured with a parallel-plate plastometer whereby a cylindrical specimen was deformed at constant load between two parallel plates whose distance apart was measured as a function of time. The viscosities were derived from the deformation–time curves obtained. Novolaks were shown to be Newtonian liquids of high viscosity. The viscosity is highly sensitive to moisture content, falling exponentially as the water content rises. 5% of water causes a 1000-fold decrease of viscosity from that of the dry resin. Over the range studied the viscosity-temperature relation is of the usual exponential type,

$$\eta = Ae^{E/RT}$$

and the activation energies for viscous flow, E, are in the 50–70 k.cal./mole range. Log (viscosity) *versus* $^1/_T$ curves were drawn for a series of carefully dried novolak resins and softening points were measured by the 'ball and ring' test for these same resins. It was found that the

softening point is the temperature at which the viscosity has a fixed value of about 8600 poises.

Several new or revised British Standard Specifications have been published defining test conditions and results,[38] and an interim report has been issued on a comparison of tests on miniature specimens cut from industrial mouldings with those on standard specimens.[39] In some cases correlation was reasonably good but it was concluded that further modifications in methods and apparatus were necessary to improve the consistency of the results and enable tests to be developed for incorporation in rigid specifications.

Applications

Many patents have been issued on the modification and application of phenoplastics for specific purposes. It is difficult to select the developments most worthy of mention, and the processes summarized in the following paragraphs form only a small fraction of those patented during the period under review. In many cases where patents describe the use of some new modifying agent it is not clear whether the motive is the utilization of an otherwise waste by-product, or the attainment of improved properties.

High impact strength mouldings can be made by incorporating up to 50% of butadiene–acrylonitrile copolymers. Certain mixtures of nitrile rubbers with phenolic resins give mouldings with impact strengths comparable with those of fabric-filled phenoplastics.[40,41]

Adhesives have again received considerable attention. Rhodes' studies of resorcinol–formaldehyde resins have continued,[42] attention being given to application methods such as that of applying the resin to the surfaces to be bonded, drying, and then applying a setting agent containing reactive methylol groups, followed by cold setting under pressure. An interesting method of obtaining improved adhesion by molecular orientation has been described by Jamieson and Barton.[43] A heat-hardenable phenolic resin is compounded with polyvinyl butyral or other acetal in warm alcoholic solution, and made into a film by extrusion, calendering or casting. Molecular orientation of the film is effected by stretching in two directions parallel to the plane of the sheet. Stretching may be achieved by extruding a tube sealed at one end and inflating to give the desired film thickness.

An interesting development in the production of laminates is the use of non-woven fabrics.[44] These have a random distribution of fibres giving equal strengths in all directions in the plane of the fabric. They are suitable for use as fillers in both high- and low-pressure laminates and cost 10–15% less than woven fabrics of comparable strength. The laminates have improved water resistance and therefore electrical properties, high impact strength and good punching qualities and can be machined at much higher speeds than woven-fabric laminates.

Cation-exchange resins have been studied from the physico-chemical point of view by Heymann and O'Donnell.[45] They measured the equilibrium between the resin and electrolytes at various p_H values, and the electrical conductivity of the swollen resin containing various cations.

The results suggest that groups more weakly acid than the sulphonic groups come into action and take part in the exchange above $p_H \sim 3{\cdot}5$, probably carboxyl and phenolic hydroxyl groups. The hydrogen resins are fairly good electrical conductors; those with metal ions are much less good, and the alkali metal resins have a maximum resistance at $p_H \sim 3{\cdot}5$. Ion-exchange theory has also been discussed in a book published during 1949.[46]

Amongst the wide range of applications of ion-exchange resins the following have been recently described; the separation of zirconium and hafnium,[47] the separation of basic amino-acids,[48] the production of formaldehyde free from formic acid,[49] and the treatment of peptic ulcers.[50] The last use depends on a specific inhibiting action on pepsin even in high acid concentrations, combined with some neutralization of stomach acidity.

Miscellaneous aromatic polycondensation plastics

Lignin-based plastics have received some further attention, the most usual manufacturing procedure being to condense lignin or lignin-containing waste wood products with other resin forming materials such as phenols, urea and aldehydes.[51,52,53] Amongst their uses is the moulding of acid-resistant battery boxes.[54]

Furan resins include first those made by condensing phenolic substances with furfuraldehyde and used, for example, for laminates[55] and for glues.[56] A comprehensive study of these resins has been made in Japan by Hachihama and his co-workers.[57] Condensations in the presence of various salts, acids and alkalis were studied with comparisons of the products. Ammonia and other alkaline catalysts and excess phenol tend to give soluble resins, whereas hydrochloric acid and excess furfuraldehyde give insoluble resins. The structures of the various resins were determined by methylation and oxidation.

The second type of furan resins is derived from furfuryl alcohol by its polymerization with or without other resin-forming substances, such as urea–aldehyde resins[58] or maleic anhydride.[59] The furfuryl alcohol resins are valuable for their chemical resistance against corrosion by acids and alkalis. The commercial production of furfuraldehyde from vegetable waste and its uses, including the synthesis of nylon through adiponitrile, have been reviewed.[60]

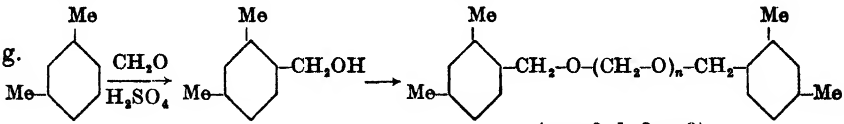
The alkylphenol–acetylene resins made in Germany during the war under the name 'Koresin' have now been described in detail.[61] The reaction takes place in an autoclave at 210° C. with zinc naphthenate as catalyst, and the product is very effective as a tackifier for synthetic rubber. Its bromination, acetylation and pyrolysis provide evidence that the *p-tert.*-butylphenol–acetylene resin is a substituted acetaldehyde.[62]

Aromatic hydrocarbon–formaldehyde resins received considerable attention in Germany during the war by Wegler and his colleagues. He has now written a comprehensive review of this work.[63]

Other interests have mainly been in the use of hydrocarbon fractions mixed with phenols and aldehydes before condensation and exerting a plasticizing action,[64] and no serious study of these resins has previously

been made. Wegler studied the condensation of many aromatic hydrocarbons with formaldehyde using acid catalysts.[65] Reactive hydrocarbons such as naphthalene and anthracene give mainly oxygen-free condensates, but most other aromatic hydrocarbons give oxygen-containing resins, particularly if relatively low temperatures, low acid concentrations and excess formaldehyde are used. With xylene, especially *m*-xylene, oxygen contents of over 16% are obtained, the benzene nuclei being joined by ether and formal linkages:

e.g.



(n = 0, 1, 2 or 3)

Many such intermediates were isolated by Wegler by fractional distillation. The particular acid catalyst is not of much significance but sulphuric acid was mainly used. Typical reaction conditions are with a 1·7 molar excess of formaldehyde and 60% of sulphuric acid, based on the xylene weight, heated for eight hours at 125° C. The lower acid layer is then run off, a little sodium carbonate added to the top layer and unreacted xylene distilled from it leaving the resin. *m*-Xylene reacts considerably faster than the other isomers so that if a crude mixture is used under conditions of partial reaction the resins are mainly derived from the more reactive isomers. Such resins, 'XF Resins,' were produced to the extent of some 1000 tons per annum by I.G. Farbenindustrie during the war and were used mainly as a cheaper and more easily available substitute for phenolic resins for blending with nitrocellulose and oil-drying lacquers.[65,66]

The resins have a low molecular weight (degree of polymerization, 6–8). They can be hardened by heating, and modified by further reaction with phenols, novolaks, alcohols, sulphonamides, natural resins, alkyds containing carboxyl groups and drying oils. Their reactivity is due to the cleavage of both formal and ether groups. *m*-Xylene is bifunctional under mild conditions although under rigorous conditions reaction can take place in any position in the nucleus so that cross-linking can occur. This polyfunctionality enables yields of over 100% to be obtained based on the hydrocarbon used.

Hardening takes place under pressure at 170° C. with 0·1% *p*-toluenesulphonic acid as catalyst. Without pressure formaldehyde is lost and hardening does not occur even at 220° C. The secondary reactions with other substances are mostly carried out at about 140° C. with 0·2% of *p*-toluenesulphonic acid as catalyst.

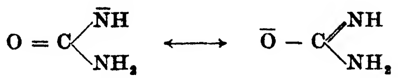
An aromatic hydrocarbon–formaldehyde resin, Claromene, is now being made in this country.

Aminoplastics

Urea–formaldehyde plastics

Crowe and Lynch[67] have made polarographic studies of the early stages of the alkali-catalysed urea–formaldehyde reaction. They

showed that the reaction was reversible and calculated the equilibrium constants. In 0·05N-lithium hydroxide, a dilute (0·004M.) monomethylol-urea solution is 90% decomposed to urea and formaldehyde. Crowe and Lynch postulated that formaldehyde in aqueous solution was normally hydrated and that the amount of electroreduction was a measure of its dehydration rate. High temperature (80° C.) and high p_H (13) favour dehydration. At 25° C. and p_H 12·7 the formaldehyde is about 41% dehydrated, but at p_H 8·7 it is only 1·2% dehydrated. This kinetic study showed that both dehydration of formaldehyde and the assumption of the formation of a urea anion,

 (resonance forms)

are necessary to account for the observed increase of the urea formaldehyde reaction rate with increase of p_H. Increase of temperature probably affects the rate of dehydration of formaldehyde without markedly changing the rate of formation of this anion of urea. p_H change affects both factors, and high p_H is thus doubly advantageous in providing both reactants : the urea anion and dehydrated formaldehyde. The effective energy of activation for the urea–formaldehyde reaction at p_H 12·7 was found to be 15·9 k.cal/mole, in agreement within experimental error with Smythe's[68] value of 14·7 k.cal/mole.

Another study[69] of the urea–formaldehyde condensation in which viscosity–time graphs were drawn and heats of condensation measured suggested that the same types of reaction were repeated at each stage of the building up of various cyclic intermediate compounds.

The manufacture of urea has been discussed in some detail,[70] and some variations on the normal low-temperature alkaline condensation with formaldehyde have been described. These include reaction at 75° C. and p_H 8 with 60% formaldehyde solution, the latter being in 5 or 6 molar excess[71] and carrying out the initial reaction under acidic conditions followed by neutralization and further addition of urea.[72,73] For stabilizing aqueous urea–formaldehyde resins, neutralization[74] and the addition of dicyanodiamide–urea–formaldehyde polycondensates have been recommended.[75] The heat conversion of urea–formaldehyde resins during moulding may be catalysed by the guanidine salt of an aromatic sulphonic acid, which although causing rapid hardening at 125–165° C., is wholly inactive in the cold.[76]

There have recently been some new applications for urea–formaldehyde resins. The foamed resin 'Fuff' has found effective use as 'snow' in film studios, and other suggested uses are for heat insulation, for chromatographic adsorption and for packing glassware.[77,78] Shackleton[79] has described the solidification of petrol by dispersing it as an emulsion in an aqueous urea–formaldehyde mixture catalysed with ammonium thiocyanate, whereupon it sets to a solid, even though the composition by volume is 94·5% petrol, 2·75% water and 2·75% true solids. A plant for solidifying 2000 gal. petrol per hour was erected in 1944. The product is not set on fire by tracer bullets or shell fragments. The petrol may be recovered by distillation or simply by pressing. If the water and

petrol are allowed to evaporate a useful porous expanded material remains.[79] Besides such well established uses as crease-proofing textiles and impregnating wood, urea–formaldehyde resins have been suggested for impregnating plaster of Paris,[80] and in conjunction with polyvinyl butyral for calendering on to paper and textiles,[81] and with carbon black filler as the heating element in blankets and flying suits.[82]

Melamine plastics

Melamine is mainly prepared by heating cyanamide or dicyanodiamide with ammonia, but may also be made by heating urea with ammonia at 300° C. under pressure or by heating cyanamide with molten potassium thiocyanate and potassium carbonate at about 220° C. in an open vessel for half an hour.[83]

There has been little theoretical work on the formation of melamine resins, but a number of patents have given details of advantageous modifications of procedure. Polycondensation is typically carried out with an excess of formaldehyde (2–8 moles per mole of melamine) at p_H 6–10 and temperatures of around 80° C. For rapid dehydration spray-drying at about 200° C. may be used.[84] Melamine–formaldehyde condensates containing an abundance of methylol groups may have these etherified by warming to 50° C. with an alcohol and a mineral acid catalyst,[85] and these ethers may be converted to esters by warming with organic acids.[86] Hardening catalysts may be latent acids such as ammonium borate or fluorosilicate,[87] and they may have a plasticizing action as well, such as monocresyl glyceryl chlorohydrin.[88]

Applications of melamine resins are varied and increasing. The absence of papers on their chemistry is surprising in view of their growing importance in recent years. Applications mentioned in recent patents and to which references will be found in the abstract literature include bonding wood laminae, surfacing wood, bonding paper laminates, impregnating and coating textiles for improving their light-fastness and crease-resistance, for anti-tracking electrical insulation, for making brake linings and moulding compositions and as a curing agent for phenolic resins. For a number of these applications, composites of melamine and other resins are recommended.

Other amine–aldehyde polycondensates

Amino-acid amides react with formaldehyde to give resins[89] as do many guanamine and triazine derivatives. Polyamines such as diethylenetriamine or tetraethylenepentamine form anion-exchange resins with formaldehyde, furfuraldehyde or sugars.[90,91] Ion-exchange resins can also be made by the interaction of primary arylamines and carbon monoxide with an acid catalyst at 250° C., and 3000 atm. pressure.[92]

Polyesters

An important concept which has been applied to linear copolyesters[94] is that of mixed crystal formation in high polymers.[93] Fuller[94] prepared copolyesters from 10-, 11- and 12-membered aliphatic dicarboxylic acids with ethylene glycol. They were cold-drawn into strong fibres which gave X-ray diffraction patterns similar to those of many simple linear

polyesters. The average fibre-period was 17·83 A. equal within experimental error to the mean of the three repeating lengths of the pure polyesters.

The method of curing saturated linear polyesters with free-radical catalysts, which was discussed in last year's Report,[95] has been used for making rubber-like products. The vulcanization with benzoyl peroxide takes place more readily if about 3% of maleic acid is included in the dibasic acid reactant. With 5% of benzoyl peroxide vulcanization may be effected by heating for 5 min. at 135° C. and vulcanizates with good tensile strength and resistance to oil, ozone, light and heat can be made suitable for electrical insulation.[96,97,98]

A vigorous development of the saturated polyethylene terephthalate, Terylene, and related polymers is taking place. This polymer may be spun from the melt at 280° C. into filaments, which when cold-drawn 470% at 60° C. in water give a yarn of strength 3·2 g./denier and 16·5% elongation.[99] The pigmenting, dyeing in the presence of a phenolic or other swelling agent, sizing with other resins, and heat treatment of this polymer have been described.[100] Polyethylene terephthalate may also be fabricated into monofilaments,[101] and into films by casting from a solvent[102] or a melt,[103] and the film may be oriented by drawing or rolling to improve its mechanical properties and chemical resistance. Stabilization against degradation can be effected by incorporating small proportions of monofunctional compounds, such as benzoic acid, with the reactants.[104] On the other hand, degradation for recovery of terephthalic acid from scrap material may be caused by hydrolysis with a mineral acid or by boiling with a large excess of glycol.[105]

Polyethylene terephthalate may be moulded by compression or injection methods, preferably with cooling of the mouldings to around 130° C. before opening the mould.[106] Polyethylene terephthalate yarn, on the other hand, may be used as a reinforcing filler for plastic or rubber articles.[107] These polymers may be blended with polyamides and polyurethanes by melting together.[108] Several related polymers have also been shown to have fibre-forming properties, including those from glycols with symmetrical naphthalene dicarboxylic acids and with various symmetrical *p*-di-arylcarboxylic acids[109,110]: e.g. $CO_2H{\cdot}C_6H_4{\cdot}R{\cdot}C_6H_4{\cdot}CO_2H$, where $R = O$; $O{\cdot}CH_2$; S; $S{\cdot}CH_2{\cdot}CH_2{\cdot}S$; $NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH$; $O{\cdot}C_6H_4{\cdot}O$; $O{\cdot}CH_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}O$. Similarly the polyesters made by heating linear *para*-substituted hydroxycarboxylic acids are fibre-forming.[111]

The unsaturated linear polyesters are used mainly for copolymerization with olefinic monomers. The principal acid component of such polyesters is maleic anhydride. This chemical is now produced on a substantial scale (about 4500 tons in U.S.A. in 1947[112]) by air-oxidation of benzene over vanadium pentoxide at 450° C., or as a by-product of the oxidation of naphthalene to phthalic anhydride. It can also be made by oxidizing crotonaldehyde with air.[113]

Typical products of this group are polyesters such as diethylene glycol maleate phthalate copolymerized with monomers such as styrene, diallyl

maleate or phthalate.[114] The polyesters may be stabilized by the addition of small amounts of polyfunctional alcohols during manufacture.[115] Closely related to the glycol polyesters are those made from castor oil and maleic anhydride, which with styrene copolymerize in a similar manner and are of particular value for electrical insulation purposes.[116] Some studies of the catalysis of the curing of these resins have recently been made,[117] and their use for bonding sawdust,[118] making cellular materials[119] and low-pressure laminating[120] have been described.

Polyamides

Polyamides are primarily of interest as fibre-forming materials rather than as plastics, but they are finding some applications in the latter field and recent developments will therefore be briefly reviewed. The absorption of water and formic acid by nylon has been studied by King[121] by measurements of the dielectric constants, rigidity moduli, swelling, and heats of wetting and absorption. Data on the increased dielectric constant and decreased rigidity indicate that the absorbate breaks inter-chain hydrogen bonds and facilitates the rotation of polar groups. Apart from this work, published papers on polyamides during the past year have been concerned mainly with new types of polyamides and their applications.

As an alternative to straight aliphatic diamines and dicarboxylic acids, diamines having ether links[122] or benzene rings[123] in their chains may be used, just as has been described above for micro-crystalline polyester manufacture. The modification of polyamides by the introduction of *N*-alkoxymethyl- and *N*-alkylthiomethyl-groups is being actively developed. The polyamide is treated with formaldehyde in the presence of an aliphatic alcohol or mercaptan and an acid catalyst.[124] These derivatives are made for their elastic fibre properties which are a consequence of the reduced hydrogen bonding between the chains, and also as adhesives either for making laminated products of high shear strength and water resistance,[125] or together with other resins for bonding plywood.[126] The related *N*-alkenoxymethylpolyamides made with unsaturated alcohols such as allyl alcohol can be rendered insoluble by heating with a peroxide catalyst.[127]

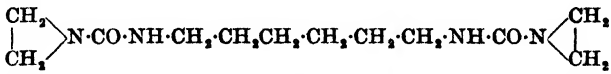
Polyamides may be plasticized with phenolic substances such as diphenyloloctadecane[128] or a compatible phenol–formaldehyde resin.[129] They may be cast as films from 40% solutions in anhydrous phenol containing a few per cent. of alkali.[130] Moulded nylon has now been used for coil forms, cams, gears, bearings, abrasion-resistant jackets for stranded steel cables, fastening devices, parts for textile machinery, and rollers for centreless grinding of aluminium tubing.[131] The most valuable properties are toughness, abrasion resistance and low coefficient of friction, combined with alkali- and heat-resistance.

Polyesteramides

These are intermediate between polyesters and polyamides, and are made by condensing dicarboxylic acids with hydroxyamines such as ethanolamines, so that the polymeric chains have alternate ester and amide linkages.[132] They are microcrystalline polymers and can be

melt-spun into filaments or formed into sheets, both of which may be oriented by cold drawing. They may be modified and partially cross-linked with di-*iso*cyanates and further cured with peroxide catalysts[133] and have been used as leathercloths, and as oil- and heat-resisting rubbers.[134]

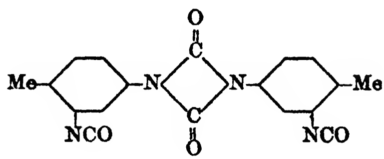
Polyethyleneimine may perhaps be mentioned here, although it is not a polyesteramide, in so far as it is also derived from ethanolamine.[135] Ethanolamine is converted by thionyl chloride and alkali to the cyclic monomer, ethyleneimine, which is explosively polymerized by acids to a linear polymer . . . $CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH$ . . . The polymer was made in Germany from 1938 to 1944 (65 tons in 1943) using traces of carbon dioxide as catalyst. Its uses included treatment of cellulose to confer water resistance. Ethyleneimine may also be reacted with hexamethylene di-*iso*cyanate to give a compound,



which readily polymerizes to a tough, transparent, infusible polymer.[136]

Polyurethanes

Polyurethanes have not, as far as is known, been manufactured since the German war-time production ceased. A few further details have become available since they were last reviewed in the 1947 Report. Toluene di-*iso*cyanate may more conveniently be used for some purposes as its dimer.[137] This was made by warming the monomer with pyridine, and is a white crystalline solid melting at 156° c., decomposing to the monomer at 160° c. and believed to have the formula



The di-*iso*cyanates were used as cross-linking agents for alkyd resins containing hydroxyl groups, e.g. trimethylolpropane adipate. Thus mixtures of 75% solutions in ethyl acetate of these two ingredients have a mix life of ten hours and form a good wood-to-wood or wood-to-iron adhesive, curing in 24 hr. at room temperature, 2 hr. at 100° c. or ½ hr. at 150° c. They are not suitable, however, for bonding large wood surfaces as in plywood manufacture, since carbon dioxide formed by reaction with the moisture in the wood cannot then escape. Related adhesives may be used for bonding metals, porcelain, phenoplastics and leather to themselves and to one another. If coated on to leather and textiles, brittle stiff finishes result owing to penetration into the fibres, but this can be avoided by first coating the leather or textile with a polymethacrylate resin. For paper coating this pretreatment is not necessary.

Moulding materials were made[137] by reacting hexamethylene di-*iso*cyanate with a mixture of 1 :4-butanediol and 2 : 6-hexanediol and

plasticizing with an *N*-alkylbenzenesulphonamide. Alternatively the toluene di-*iso*cyanate dimer, trimethylolpropane adipate and woodflour may be worked on hot rolls at 105° C. until uniform, followed by moulding at 165° C. This is possible since only two of the *iso*cyanate groups react at 105° C. and it is necessary to heat to about 165° C. before the other two react.

Several reviews of polyurethanes have been published especially with reference to their use in lacquers,[138] and correlation of their structure with fibre-forming properties has been attempted.[139]

Silicones

Large numbers of patents are being issued covering variations of procedure for the manufacture, processing, stabilizing and curing of silicones. The various silicone products such as resins, rubbers and greases are made by the controlled hydrolysis with accompanying polymerization of organo-halogenosilanes or -ethoxysilanes. Both the halogeno- and ethoxy- derivatives can be made with Grignard reagents acting on, e.g. silicon tetrachloride or silicochloroform,[140] and on ethyl orthosilicate[141] respectively. Organo-fluorosilanes which are useful for the preparation of insecticides and textile waterproofing agents may be prepared from the corresponding chloro- or bromo- silanes by interaction with antimony trifluoride.[142] The aryl- but not the alkyl-silanes can be made by the Wurtz–Fittig reaction from silicon tetrachloride and chlorobenzene or its derivatives in the presence of sodium.[143] This reaction is suitable for the laboratory but would be difficult to adapt to large-scale operations. An analogous reaction may be carried out between ethyl orthosilicate and diethyl sulphate in the presence of sodium giving diethyldiethoxysilane.[144] The corresponding reaction with ethyl chloride can be carried out over magnesium as a continuous process.[145]

The organo-silicon halides can also be made directly from organic halides and silicon. The reaction may be carried out over a silicon–cuprous chloride mass or a silicon–copper alloy at temperatures ranging from 200 to 1000° C.,[146] or over ferro-silicon at 300 to 500° C.[147] The hydrolysis of the organo-silicon halides may be carried out by controlled addition of water in a solvent with acid or alkali as catalyst,[148] or the polymerization to silicones may be brought about by heating with anhydrous alkali,[149] zinc oxide,[150] hydrated metal salts,[151] phosphorus pentoxide,[152] boric acid,[153] or anhydrous acids.[154]

The linear silicone polymers can be cured by heating with benzoyl peroxide,[155] and if vinyl or allyl groups are introduced into the silicone curing is wholly by addition polymerization.[156] Another modifying procedure is chlorination which may be carried out on the organo-silicon halide or on the silicone and improves the craze resistance and toughness.[157]

The infra-red absorption spectra of many silicones and their intermediates were examined between 2 and 20 μ. by Richards and Thompson[158] who found strikingly high intensities for many of the absorption bands. The methylpolysiloxanes showed a sharp intense band near 1265 cm.$^{-1}$ which was attributed to the rocking of the Si-Me groups, and other intense bands near 800 cm.$^{-1}$ and 1050 cm.$^{-1}$ connected with the

vibrations of the Si-C and Si-O links. The chlorosilanes had an intense band near 810 cm.$^{-1}$ due possibly to the vibration of the Si-Cl bonds, and a bond near 2200 cm.$^{-1}$ due to the stretching of Si-H links.

The uses of silicones have again been reviewed by Hardy.[159] They include exposure to methylchlorosilane vapours as for rendering the surfaces of ceramic insulators hydrophobic,[160] rendering wool non-felting[161] and water-proofing filter-papers. Colourless fluids with low viscosity coefficients can be made by shaking linear or cyclic dimethylsiloxanes with hexamethyldisiloxane and a little sulphuric acid in the cold for 16 hr. : the siloxane linkages are broken and recombined with trimethylsilyl groups as chain stoppers ; these fluids are used as lubricants, hydraulic media, shock absorbers, high-temperature bath fluids, diffusion-pump oils, mould release agents and for breaking emulsions. Silicone greases, made by milling the gels from the hydrolysis of bi- and tri-functional methylsilane intermediates, are used for sealing ignition systems, and as lubricants for low-pressure rubber-bag moulding. Silicone rubbers are made from long-chain dimethylsiloxane polymers milled with fillers and peroxides, extruded at 150° c. and cured at 200° c. ; they are used as gasket materials. Silicone resins are derived mainly from ethyl- and phenylsilane intermediates, rather than from the methyl compounds, and mixtures of the mono- and tri-functional reactants give the best results. Applications are for impregnating glass fabric, for laminating and for surface coating where heat, light or chemical resistance is important.

References

[1] Annual Abstract of Statistics, H.M.S.O.. 1949
[2] Vansheidt, A. A. and Gruz, R. I., *J. appl. Chem., USSR*, 1948, **21**, 502
[3a] Ziegler, E., *Mh. Chem.*, 1948, **78**, 334
[3b] Ziegler, E. and Zigeuner, G., ibid., 1948, **79**, 42
[3c] Ziegler, E. and Lüdde, H., ibid., 55
[3d] Zigeuner, G. and Ziegler, E., ibid., 89
[3e] Idem, ibid., 100
[3f] Ziegler, E., ibid., 142
[3g] Ziegler, E. and Lüdde, H., ibid., 316
[3h] Ziegler, E. and Zigeuner, G., ibid., 358
[3i] Idem, *Kunststoffe*, 1949, **39**, 191
[3j] Ziegler, E., *Ost. Chem. Ztg.*, 1948, **49**, 92
[4] Ziegler, E. and Zigeuner, G., *Mh. Chem.*, 1948, **79**, 363
[5] Becker, B. and Barthel, E., ibid., 1947, **77**, 80
[6a] Ruderman, I. W., *J. Amer. chem. Soc.*, 1948, **70**, 1662
[6b] Ruderman, I. W. and Fettes, E. M., ibid., 1949, **71**, 2264
[7] Sprengling, G. R. and Freeman, J. H., abstracted in *Chem. Engng. News*, 1949, **27**, 2924
[8] Sprung, M. M. and Gladstone, M. T., *J. Amer. chem. Soc.*, 1949, **71**, 2907
[9] Finn, S. R. and Rogers, L. R., *J. Soc. chem. Ind.*, 1948, **67**, 51
[10a] Müller, H. F. and Müller, I., *Kunststoffe*, 1948, **38**, 25
[10b] Idem, ibid., 221 ; Annual Reports, 1948, **33**, 354
[11a] Zinke, A. and Hanus, F., *Mh. Chem.*, 1948, **78**, 311
[11b] Zinke, A. and Ziegler, E., ibid., 317
[11c] Ziegler, E. and Hontschik, I., ibid., 325
[11d] Zinke, A. and Pucher, S., ibid., 1948, **79**, 26
[11e] Ziegler, E. and Kohlhauser, R., ibid., 92
[11f] Zinke, A. *et al.*, ibid., 438
[12a] Hultzsch, K., *Angew. Chem.*, 1948, **60**, 179
[12b] Idem, *Kunststoffe*, 1948, **38**, 65

[12c] Idem, *Chem. Ber.*, 1949, **82**, 16
[12d] Idem., *Kunststoffe*, 1949, **39**, 57
[12e] Idem, *Angew. Chem.*, 1949, **61**, 93
[13] Messing, R. F. and Keary, W. V., *Chem. Industr.*, 1948, **63**, 43, 234
[14] Harman, R. A. and Solway Process Co., U.S.P. 2,382,148 ; Porter, F. and Solway Process Co., U.S.P. 2,392,875 ; Porter, F. and Allied Chemical and Dye Corpn., U.S.P. 2,437,921 ; Krieble, R. H., Denton, W. I. and Socony Vacuum Oil Co. Inc., U.S.P. 2,439,812
[15] Socony Vacuum Oil Co., *Chem. Trade J.*, 1949, **125**, 392
[16] United International Research Inc., ibid., **124**, 402
[17] Luten, D. B., de Benedictis, A. and Shell Development Co., U.S.P. 2,435,087 ; Mohrman, H. W. and Monsanto Chemical Co., U.S.P. 2,433,143
[18] Cislak, F. E., Otto, M. M. and Reilly Tar and Chemical Corpn., U.S.P. 2,432,062–3
[19] Skeen, J. R., *Chem. Engng. News*, 1948, **26**, 3344
[20] Hall, J. L., U.S.P. 2,384,028 ; Hochwalt, C. A., Monsanto Chemical Co. *et al.*, U.S.P. 2,434,850
[21] Sahasrabudhey, R. H. and Kalyanasundaram, A., *Proc. Indian Acad. Sci.*, 1948, **27**, 366
[22] Nystrom, R. F., Yanko, W. H. and Brown, W. G., *J. Amer. chem. Soc.*, 1948, **70**, 441
[23] Pritchett, E. G. K., Barnett, G. and Bakelite Ltd., B.P. 615,488
[24] Bakelite Corpn., B.P. 613,016
[25] Bakelite Ltd., B.P. 615,335
[26] Westinghouse Electric International Co., B.P. 608,052
[27] Borden Co., B.P. 608,940
[28] Bakelite Corpn., B.P. 622,657
[29] Bakelite Ltd., B.P. 604,079
[30] Guzzetti, A. J., *Brit. Plastics*, 1949, **21**, 273
[31] Goddard, F. C., ibid., 170
[32] Kuntze, W. and Pfieffer, F., *Kunststoffe*, 1940, **30**, 293 ; Le Rolland, P., *Industr. plast.*, 1945, **1**, 68 ; Sorin, M., ibid., 1947, **3**, 367
[33] Norelli, P., *Mod. Plastics*, 1948, **25**, No. 3, 121
[34] Bernhardt, E. C., ibid., No. 2, 123
[35] Barwell, F. T. and Pepper, K. W., *Trans. Faraday Soc.*, 1946, **42B**, 275
[36] Bowman, R. P., Fitzgerald, J. S. and Jensen, F. M., *J. Coun. Sci. industr. Res. Aust.*, 1947, **20**, 503
[37] Dienes, G. J., *J. Colloid Sci.*, 1949, **4**, 257
[38] B.S. 1314 : 1946 ; 1321 : 1946 ; 1323 : 1946 ; 771 : 1948
[39] B.S. 1330 : 1946
[40] Shepard, A. F. and Boiney, J. F., *Mod. Plastics*, 1946, **24**, No. 2, 154
[41] Newberg, R. G. *et al.*, *Rubb. Age, Lond.*, 1948, **62**, 533; Powers, P. O., *Chem. Engng. News*, 1949, **27**, 13
[42] Rhodes, P. H., U.S.P. 2,385,372–4 ; 2,432,544 ; 2,437,710 ; B.P. 599,683 ; 613,106
[43] Jamieson, A. M., Barton, E. E. and Bakelite Ltd., B.P. 601,496
[44] *Mod. Plastics*, 1949, **26**, No. 9, 70
[45] Heymann, E. and O'Donnell, I. J., *J. Colloid Sci.*, 1949, **4**, 395
[46] "Ion-Exchange, Theory and Application" (Academic Press Inc., 1949)
[47] Street, K. and Seaborg, G. T., *J. Amer. chem. Soc.*, 1948, **70**, 4268
[48] Hems, B. A., Page, J. E. and Waller, J. G., *J. Soc. chem. Ind.*, 1948, **67**, 77
[49] Zowader, H., *Chem. Engng. Progr.*, 1949, **45**, 279
[50] Rohm and Haas Co., *Chem. Trade J.*, 1949, **125**, 240
[51] Loughborough, W. K., U.S. Sec. of Agric., U.S.P. 2,442,897
[52] Kipphan, K., *Kunststoffe*, 1949, **39**, 71
[53] Sorgato, H., *Chim. et Industr.*, 1949, **61**, 345
[54] General Motors Corpn., B.P. 601,506
[55] Kline, H., *Paper Ind. & World*, 1948, **30**, 775
[56] Phillips, L. N. and Pryor, M. G. M., B.P. 609,315
[57] Hachihama, Y., Imotu, M. *et al.*, *J. Soc. chem. Ind., Japan*, 1942, **45**, 1053 ; 1943, **46**, 520, 808 ; 1944, **47**, 178, 359, 657, 824 ; 1946, **49**, 61
[58] Simons, W. G. and British Industrial Plastics Ltd., B.P. 610,302
[59] Hersh, H. I. and Owens-Illinois Glass Co., U.S.P. 2,432,890
[60] Hitchcock, L. B. and Duffey, M. R., *Chem. Engng. Progr.*, 1948, **44**, 669 ; *Canad. Chem.*, 1948, **32**, 718

[61] Zoss, A. O., Hanford, W. E. and Schildknecht, C. E., *Ind. Eng. Chem.*, 1949, **41**, 73
[62] Le Maistre, J. W. and Seymour, R. B., *J. Amer. chem. Soc.*, 1948, **70**, 1776
[63] Wegler, R., *Angew. Chem.*, 1948, **60 A**, 88
[64] Rostler, F. S., Bornstein, L. and Wilmington Chemical Co., U.S.P. 2,439,824; Narracott, E. S., Rowland, K. J. and Anglo-Iranian Oil Co., Ltd., B.P. 612,416
[65] CIOS Report No. XXIX–14, p. 74
[66] Thurston, J. T., FIAT Report No. 950
[67] Crowe, G. A. and Lynch, C. C., *J. Amer. chem. Soc.*, 1948, **70**, 3795; 1949, **71**, 3731
[68] Smythe, L. E., *J. phys. Colloid Chem.*, 1947, **51**, 369
[69] Vaskevitsch, D. N. and Sabun, L. A., *J. gen. Chem., USSR*, 1944, **14**, 292
[70] Frèjacques, M., *Chim. et Industr.*, 1948, **60**, 22
[71] Du Pont Co., U.S.P. 2,467,212
[72] British Resin Products Ltd., B.P. 627,167
[73] *Industr. Chem. chem. Mfr.*, 1948, **24**, 448
[74] American Cyanamid Co., B.P. 614,307
[75] Berlin, A. A. and Izyumov, B. D., *J. appl. Chem., USSR*, 1946, **19**, 23
[76] Cordier, D. E. and Libbey-Owens-Ford Glass Co., U.S.P. 2,446,867
[77] Expanded Rubber Co., *J. sci. Instr.*, 1948, **25**, 422
[78] van Buskirk, E. C. and Surland, C. C., *Chem. Engng. Progr.*, 1948, **44**, 803
[79] Shackleton, L. R. B., *Industr. Chem. chem. Mfr.*, 1949, **25**, 423
[80] Delmonte, J., *Mod. Plastics*, 1948, **25**, No. 8, 98
[81] Leekley, R. M. and du Pont Co., U.S.P. 2,432,242
[82] Edgar, D. E., Sullivan, D. J. and du Pont Co., U.S.P. 2,386,095
[83] Jayne, D. W., Day, H. M. and American Cyanamid Co., U.S.P. 2,377,499
[84] Monsanto Chemical Co., B.P. 601,983
[85] Société Chem. Ind., Basel, B.P. 611,013
[86] Idem, B.P. 611,012
[87] Harris, R. R. and American Cyanamid Co., U.S.P. 2,388,143
[88] Hayward, J. E. H., Calderbank, P. H. and Bakelite Ltd., B.P. 611,562
[89] Marvel, C. S., U.S.P. 2,436,363
[90] Sussman, S. and Permutit Co., U.S.P. 2,392,105 and 2,442,989
[91] Bowman, P. I., Burrell, H. and Heyden Chemical Corpn., U.S.P. 2,388,235
[92] Buckley, G. D., Ray, N. H. and I.C.I. Ltd., B.P. 615,363
[93] Bunn, C. W. and Peiser, H. S., *Nature*, 1947, **159**, 161
[94] Fuller, C. S., *J. Amer. chem. Soc.*, 1948, **70**, 421
[95] ANNUAL REPORTS, 1948, **33**, 360
[96] Biggs, B. S., Erickson, R. H. and Fuller, C. S., *Ind. Eng. Chem.*, 1947, **39**, 1090
[97] Fuller, C. S. and Bell Telephone Laboratories, Inc., U.S.P. 2,388,319; 2,442,330; 2,448,585
[98] Frosch, C. J. and Bell Telephone Laboratories Inc., U.S.P. 2,388,318; 2,448,584
[99] Whinfield, J. R. and Dickson, J. T., B.P. 603,827
[100] I.C.I. Ltd. *et al.*, B.P. 609,943; 609,945; 609,946; 609,948; 610,096; 610,137; 610,167; 610,171; 610,183; 610,184
[101] Byers, J. S., Swallow, J. C. and I.C.I. Ltd., B.P. 609,796
[102] Swallow, J. C., Baird, D. K., Ridge, B. P. and I.C.I. Ltd., B.P. 610,202
[103] Swallow, J. C. and I.C.I. Ltd., B.P. 609,797
[104] Lewis, J. R., Reynolds, R. J. W. and I.C.I., Ltd., B.P. 610,138
[105] Heath, R. L. and I.C.I. Ltd., B.P. 610,135; 610,136
[106] Byers, J. S., Swallow, J. C., Walter, J. M. and I.C.I. Ltd., B.P. 609,795
[107] Ridge, B. P., Watts, J. T. and I.C.I. Ltd., B.P. 610,170
[108] Dickson, J. T., Reynolds, R. J. W. and I.C.I. Ltd., B.P. 610,140
[109] I.C.I. Ltd. *et al.*, B.P. 604,073; 604,074; 604,075
[110] Birtwistle, W. K., B.P. 609,792
[111] Cook, J. G., Dickson, J. T., Lowe, A. R. and I.C.I., Ltd., B.P. 604,985
[112] Skeen, J. R., *Chem. Engng. News*, 1948, **26**, 3684
[113] British Celanese Ltd., B.P. 613,775
[114] D'Alelio, G. F. and General Electric Co., U.S.P. 2,441,799; 2,445,764; British Thomson-Houston Co., Ltd., B.P. 613,650
[115] Rothrock, D. A., Coyne, R. F. and Resinous Products & Chemical Co., U.S.P. 2,437,046; 2,437,232
[116] British Thomson-Houston Co. Ltd., B.P. 592,400; Westinghouse Electric International Co., Ltd., B.P. 605,706

[117] Patterson, D. G. and Robinson, F. D., *India Rubb. World*, 1948, **118**, 811
[118] Gabriel, A. E., *Mod. Plastics*, 1948, **25**, No. 8, 145
[119] U.S. Rubber Co., B.P. 605,023
[120] Minnear, F. L., *India Rubb. World*, 1948, **119**, 348; Bakelite Ltd., B.P. 603,562
[121] King, G., *J. Colloid Sci.*, 1947, **2**, 551
[122] Ellery, E. and I.C.I. Ltd., B.P. 615,954
[123] Du Pont Co., B.P. 610,264
[124] Cairns, T. L. *et al.* and du Pont Co., U.S.P. 2,430,859; 2,430,860; 2,430,866; 2,430,867; 2,430,875; 2,430,907; 2,430,908; 2,430,910; 2,430,923; 2,430,953, 2,441,057; B.P. 608,332; 608,335; Cairns, T. L. *et al.*, *J. Amer. chem. Soc.*, 1949, **71**, 651
[125] Hoover, F. W. and du Pont Co., U.S.P. 2,430,933
[126] Rothrock, H. S. and du Pont Co., U.S.P. 2,430,950
[127] I.C.I. Ltd., B.P. 604,902
[128] Balthis, J. H. and du Pont Co., U.S.P. 2,374,069
[129] I.C.I. Ltd., B.P. 605,767
[130] Watkins, W. W. and du Pont Co., U.S.P. 2,431,783
[131] Powers, P. O., *Chem. Engng. News.*, 1949, **27**, 13; Kline, G. M., *Ind. Eng. Chem.*, 1949, **41**, 2132
[132] Kropa, E. L. and American Cyanamid Co., U.S.P. 2,240,416; Frosch, C. J. and Bell Telephone Laboratories Inc., U.S.P. 2,386,454
[133] I.C.I. Ltd. *et al.*, B.P. 599,905; U.S.P. 2,431,921
[134] Harper, D. A., *I.R.I. Trans.*, 1948, **24**, 181
[135] *Mod. Plastics*, 1948, **26**, No. 3, 130
[136] O.P.B. Report No. 46,961 (Scientific and Industrial Reports, 1947)
[137] Lockwood, W. H., FIAT Report No. 1301
[138] Thinius, K., *Farbe u. Lack*, 1948, **54**, 227, 275, 302; *Kunststoffe*, 1948, **38**, 108; U.S.P. 2,396,621; Hebermehl, R., *Farben, Lacke, u. Anstrichstoffe*, 1948, **2**, 123
[139] Hill, R. and Walker, E. E., *J. Polymer Sci.*, 1948, **3**, 609
[140] McGregor, R. R., Warwick, E. L. and Corning Glass Works, U.S.P. 2,375,998; Hyde, J. F. and Corning Glass Works, U.S.P. 2,438,478; Barry, A. J. and Dow Chemical Co., B.P. 618,403
[141] McGregor, R. R., Warwick, E. L. and Corning Glass Works, U.S.P. 2,380,057
[142] Pletcher, D. E., Nutting, H. S. and Dow Chemical Co., U.S.P. 2,436,777
[143] Bassett, E. A. *et al.*, *J. Soc. chem. Ind.*, 1948, **67**, 177; Bowman, A. *et al.* and I.C.I. Ltd., B.P. 613,648
[144] Taylor, A. G. and Albright & Wilson Ltd., B.P. 607,811
[145] Meadowcroft, A. E., Shaw, C. and Smith, W. E., B.P. 609,841
[146] Rochow, E. G. *et al.* and General Electric Co., U.S.P. 2,383,818; 2,389,931; 2,443,902; 2,447,873
[147] Dow Chemical Co., B.P. 609,507; Riccoboni, L. and Zotta, M., *J. Soc. chem. Ind.*, 1948, **67**, 235
[148] Corning Glass Works *et al.*, U.S.P. 2,437,204; 2,439,856; 2,441,098; 2,441,320; 2,443,353; 2,446,135; B.P. 603,076; 607,253; 611,700; Dow Chemical Co., B.P. 618,459
[149] Hyde, J. F. and Corning Glass Works, U.S.P. 2,432,655
[150] Shaw, C., Smith, W. E. and Emblem, H. G., B.P. 606,301
[151] Wright, J. G. E., Marsden, J. and General Electric Co., U.S.P. 2,389,477
[152] Corning Glass Works *et al.*, U.S.P. 2,435,147
[153] Idem, U.S.P. 2,431,878; British Thomson-Houston Co. Ltd., B.P. 605,218
[154] Campbell, A. H. and Revertex Ltd., B.P. 609,324
[155] Warrick, E. L. and Corning Glass Works, B.P. 608,955; 608,956; 610,152; General Electric Co., *et al.*, U.S.P. 2,448,530; 2,448,565
[156] British Thomson-Houston Co, B.P. 618,451; Hurd, D. T. and Roedel, G. F., *Ind. Eng. Chem.*, 1948, **40**, 2078
[157] British Thomson-Houston Co., B.P. 610,898; 610,899; 611,494; Corning Glass Works *et al.*, U.S.P. 2,435,148
[158] Richards, R. E. and Thompson, H. W., *J. chem. Soc.*, **1949**, 124
[159] Hardy, D. V. N., *Paint Manuf.*, 1949, **19**, 230
[160] Halls, E. E., *Elect. Manuf.*, 1949, **5**, No. 1, 25
[161] Alexander, P., Carter, D. and Earland, C., *J. Soc. Dy. Col., Bradford*, 1949, **65**, 107

PLASTICS FROM NATURAL POLYMERS (T. N. Parkin, B.Sc., A.R.I.C.)

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UNDER the stimulus of competition from the newer thermoplastics, much progress is being made in the manufacture of plastics based on cellulose organic esters and ethers. The low cost of some of these competitors has provided an added incentive for improving the speed and efficiency of cellulose ester manufacture as the most promising method of cheapening production, and reference will be made below to processes giving greater speed in pre-treatment, esterification, ripening and stabilization. The fact that the cellulosic plastics now have to compete with a variety of synthetics, each showing excellence in some particular respect, has accelerated the improvement of their properties in several directions. Improved water resistance and dimensional stability are being obtained by the use on an increasing scale of cellulose acetates of high acetyl value and of esters of higher fatty acids (including mixed esters); for cinema-film, cellulose triacetate seems likely before long to supplant cellulose nitrate entirely. Progress has also been made in improving the clarity, light-stability and heat-stability of cellulose derivative plastics, and various methods of cross-linking cellulose derivatives to obtain infusible products have been described. The fabrication of cellulosic plastics has also gained from the adoption of methods used extensively on the newer plastics, e.g. dry methods of incorporating plasticizers and of extrusion.

The research being pursued so vigorously by the manufacturers with a view to improving and cheapening their products is paralleled by much fundamental research into the structure and behaviour of the raw materials of the industry, and the development of improved methods of testing and analysis both by manufacturers and by research schools and public bodies.

Some idea of the present economic position of the cellulose-derivative industry can be obtained from the following figures (in thousands of pounds weight) of total production in U.S.A. for the first six months of 1949 and for the corresponding period of 1948.[1]

	Jan. to Jun. 1948	Jan. to Jun. 1949
Cellulose organic ester:		
Foils	3070	3287
Thicker continuous sheets	3408	3682
Rods, tubes and discontinuous sheets	1575	2161
Moulding and extrusion compositions	23096	25309
Cellulose nitrate:		
Sheets	3857	3571
Rods and tubes	1668	738
Other cellulosic plastics	4164	4589

It is significant that in a country where competitive plastics are more plentiful and cheaper than anywhere else, the consumption of every type of cellulosic plastic except cellulose nitrate shows an increase over that

for the corresponding period of the preceding year. In Great Britain, although published figures are not available, it is known that consumption is also increasing.

In the cellulose nitrate plastics field no striking developments are recorded; this is not surprising in view of the already low cost of cellulose nitrate and the fact that, apart from inflammability, cellulose nitrate appears ideally suited for its task. In protein plastics there is evidence of research directed to improving on the usual formaldehyde method of cross-linking casein, and investigating potential raw materials other than casein.

Cellulose derivatives suitable for plastics

Research directed to finding native raw materials suitable for the manufacture of cellulose derivatives continues. In Germany, where re-afforestation is necessary after the war, much information is being accumulated as to the yield, degree of polymerization and ease of purification of the cellulose obtainable from native trees, especially the fast-growing deciduous trees. Typical of this work is the account given by H. Haas of the fractionation products of 15 deciduous and 5 coniferous woods.[2] Abstracts in English are now available of many papers published in Japan during the war, including papers on the manufacture of pulp from various coniferous, deciduous and tropical trees,[3] and from bagasse;[4] on a microscopic study of pulping,[5] and on the nitric acid pulping process.[6] Bagasse is being made into paper in Argentina but attempts to make satisfactory cellulose acetate from it have so far failed.[7] Straw continues to invite attention, and a well-documented French account of the composition of various straws is available. The yield of cellulose was found to average about the same as in wood.[8] Up to now straw cellulose has been used in the manufacture of paper and of viscose rayon. Even in Great Britain some 2000 tons of straw per week are used in the manufacture of paper,[9] and in Germany a large manufacture of staple fibre is to be based on straw cellulose, but for cellulose derivative manufacture straw has not been considered very suitable. A novel process said to yield cellulose in suitable form has now been patented, involving anaerobic fermentation, which frees the fibre from lignin, pectin and silica, followed by a hypochlorite bleach.[10]

Progress in the pulping industry cannot be surveyed here, but a few interesting facts and publications may be mentioned. The difficulties of running a pulping process continuously have been analysed, and a method for overcoming them has been proposed: this involves maintaining a high pressure in the digestor by the continuous introduction of waste liquor.[11] It has been claimed that 90% α-cellulose with less than 5% of pentosans can be obtained from lignocellulose materials by a single-stage alkaline pressure-cook for about 20 minutes at about 200° c.[12] An interesting account has been given of the conversion of a lime-base sulphite process to a cyclic magnesia-base process, with many advantages, including a solution of the effluent problem.[13] The great variety of useful products that can be recovered from sulphite waste liquor, including tanning and dispersing agents, detergents, insecticides, alcohols, fodder-yeasts and vanillin has been discussed by J. A. Pearl.[14]

In making paper—phenol–aldehyde laminates, excellent products have been obtained by incorporating lignin in the paper during pulping and using correspondingly less phenol–aldehyde.[15] In Great Britain two small sulphite pulp mills are operating, and straw is being pulped by chlorination, after pre-treatment with alkali, and followed by further alkali treatment and bleaching.[15]

Methods of determining the molecular weight distribution in cellulosic material, which is now recognized as having an important effect on the properties of cellulose derivative plastics made from it, are being continually improved. A simplified method developed in a French laboratory consists in nitration followed by determination of the specific viscosity of the nitrate in acetone solution by the Ostwald method, immediately after solution (since degradation occurs on standing); a correction for acceleration is made in the viscosity determination, but extrapolation to infinite dilution is avoided.[16] Another method has been described in which, to avoid degradation, the viscosity of the nitrate is measured in ethyl acetate solution.[17]

Several further patents have been granted for processes directed to avoiding degradation in bleaching cellulose. In one method ozone is used with careful control of moisture content.[18] Another method uses a mild alkaline chlorine bleach followed by treatment with aqueous chlorine and excess of chlorine dioxide.[19]

Alkali hypobromite is used in a third process, preferably before or after a hypochlorite bleach.[20] For purifying unbleached sulphite pulp a method comprising treatment in succession with hot alkali, chlorine, hot alkali and hypochlorite, with neutralization after each such treatment, has been recommended.[21]

The mechanism of nitration is being investigated by Chedin and co-workers, who have found that the crystalline regions of the cellulose fibre are nitrated only by undissociated nitric acid, whereas the amorphous regions allow the entry of, and are attacked by, the various complexes formed by nitric acid with sulphuric acid. When the concentration of nitric acid was less than 95% the same degree of nitration was obtained as with the same concentration of nitric acid in admixture with sulphuric acid, whereas when the concentration of nitric acid was above 95% a lower degree of nitration was effected in the absence of sulphuric acid.[22]

A very rapid method of pre-treating pulp to facilitate acetylation has been patented. First water, then glacial acetic acid, and finally acetic acid containing the acetylation catalyst, are sucked through the pulp sheets, each step taking 10–20 seconds, after which acetylation can be carried out immediately or after standing up to 15 minutes.[23] Another method of pre-treatment, said to result in high clarity, comprises boiling the pulp with water of low mineral content, removing most of the water mechanically, and displacing the remainder by means of acetic acid.[24] The object of this treatment is evidently to minimize the so-called salt effect (referred to, e.g. by C. J. Malm[25] and H. M. Spurling[26]) caused by formation of calcium and like salts of stray carboxyl groups in the cellulose. Reference may be made here to a more general method of eliminating the salt effect in cellulose or a cellulose derivative by washing first with ordinary water at p_H 2–5 (which decomposes the salts) and then with

demineralized or distilled water.[27] The water content and pore size of cellulose for acetylation are important and a method of drying without causing shrinkage has been described.[28] A method of regulating drying on hot cylinders has been patented.[29]

The rate of esterification of the primary hydroxyl groups in cellulose has been found by a tosylation method to be about six times that for the secondary groups.[25] In an attempt to prepare cellulose trifluoroacetate by the action of trifluoroacetic acid on cellulose swollen in acetic acid, the interesting discovery was made that the trifluoroacetic acid acted as an impeller for the acetic acid, giving a chloroform-soluble cellulose acetate containing above 40% acetyl, in one hour at 50–60° C. Degradation, though not measured, was thought not to be extensive; cellulose benzoate was prepared with the same impeller.[30] Unusual methods of acetylating cellulose that have been investigated include: the use of keten with sulphuric acid or perchloric acid as catalyst (for partial acetylation in suspension)[31]; the use, in a Russian laboratory, of acetyl chloride with a picoline as catalyst[32]; and the use of sulphanilic acid or *p*-toluenesulphonic acid as acetylation catalyst (in high-temperature suspension acetylation of bleached jute fibre by means of anhydride in xylene or chlorobenzene).[33]

A significant improvement in the established method of acetylation by means of acetic anhydride in acetic acid solution with sulphuric acid as catalyst is a continuous process in which the cellulose is highly activated by treatment with hot acetic acid, or with acetic acid plus 2–7% of sulphuric acid, and esterified at an initial temperature of about 50° C.[34] In another process a striking reduction in degradation during acetylation is said to be obtained by removing and precipitating the cellulose acetate as soon as it dissolves, leaving acetylation to continue in the undissolved material by virtue of the acetylating medium which it has imbibed.[35]

In the production of cellulose triacetate, using sulphuric acid as catalyst, it is of course necessary to stabilize by removing combined sulphuric acid without reducing the acetyl content. One method of doing this is to heat the acetylation mixture for 1–30 hours at 130–85° C. after neutralizing sulphuric acid, e.g. with magnesium carbonate, or other salt of a Group II metal or of aluminium, without adding enough water to react with all the residual anhydride.[36] A patented process for obtaining triacetate in the form of an easily washed powder consists in neutralizing, e.g. with a magnesium salt, followed by dilution in two stages with acetic acid of decreasing concentration, with an intermediate heating step.[37] An alternative method of obtaining stabilized triacetate is to re-acetylate a stabilized, ripened acetate in solution by means of acetic anhydride in the absence of a catalyst.[38]

In the manufacture of acetone-soluble cellulose acetates a remarkable reduction in ripening time (from the usual 20–50 hours down to 15–45 minutes) can be obtained by ripening under pressure at a temperature of at least 125° C. In this process improved clarity is obtained by ripening in an oxygen-free atmosphere.[39] Rapid and very effective stabilization can be effected simultaneously with ripening by bringing the temperature of a neutralized primary acetylation mixture to at least 60° C. by injecting steam, adding further sulphuric acid and maintaining

the temperature for 15 minutes, after which further ripening can be carried out at about 100° C.[40] Ammonium bisulphate can be used instead of the added sulphuric acid, and very stable esters, especially suitable for moulding, are obtainable in this way.[41] A further method involves neutralizing the catalyst, heating with 25–50% (on the cellulose) of water to split off combined sulphuric acid, adding further water and ripening to the desired acetyl content at 125–190° C.[42] In cellulose acetates of high acetyl content, the stability required for moulding can readily be obtained by high-temperature stabilization in the presence of a non-ionic surface-active agent.[43] In an investigation of the mechanism of ripening it was found that the percentage of primary groups hydrolysed decreases with increase of water in the ripening bath but is independent of temperature and of the nature and amount of catalyst.[25]

Mixed esters of acetic and higher fatty acids, e.g. lauric acid, have been made by esterifying a ripened cellulose acetate with the acid chloride of the higher acid in the presence of pyridine, after activating the cellulose acetate for the further esterification by washing with hot water.[44] Cellulose acetate–butyrates containing up to 2·4 butyryl groups and 0·5 acetyl groups, and similar in stability, but superior in covering power and moisture resistance, to lacquer-grade cellulose nitrates, are now available.[45] Cellulose acetate–butyrate of high acetyl content and high molecular weight and stability (suitable for photographic films) can be obtained by esterification with a mixture of acetic anhydride and the higher acid, followed by stabilization and slight hydrolysis with hot dilute sulphuric acid, and neutralization without further hydrolysis, in the cold, with a slightly alkaline aqueous solution.[46]

Cellulose acetate of specially good clarity and freedom from colour development when moulded can be obtained in 70–80% yield from ordinary cellulose acetate by a two-stage precipitation from an acetone solution, the first fraction (containing the colour and haze-forming constituents) and the unprecipitated ester of low molecular weight being discarded.[47]

In connexion with cellulose ether production, a recent study of the autoxidation of alkali-cellulose is of great interest. In this chain-reaction, traces of transition metals such as manganese and cobalt, as well as sodium sulphide and various other autoxidizable substances and free-radical formers, accelerate the reaction and increase the depolymerization and the proportion of aldehyde groups formed, whereas silver and gold and various antioxidants show opposite effects. A tentative scheme for the reaction mechanism is outlined.[48] Various methods of controlling the depolymerization have been proposed. One method is to carry out both the formation of the alkali-cellulose and the etherification in the absence of air, any substantial depolymerization required being effected during preliminary bleaching of the cellulose.[49] In another method a controlled degree of depolymerization is obtained by carrying out the etherification in the presence of a hypochlorite, hypobromite, hypoiodite, peroxide or periodate.[50] Sodium trithiocarbonate has been used to reduce the rate of depolymerization in making alkali-cellulose for viscose manufacture.[51] Traces of iron combined with stray carboxyl groups in the cellulose have been found to reduce the heat

stability of cellulose ethers, and it is of interest that improvement in stability has been obtained by treating the ether in solution with a solid cation-exchange agent such as pectic acid or carboxymethyl cellulose to remove the iron, the carboxyl groups then being neutralized, preferably by treatment with caustic soda together with a hydroxide of a bivalent metal. Various metals were found to have a stabilizing effect.[52] The ethylation of alkali-cellulose under reduced pressure has been investigated and found advantageous.[53] Etherification has been accelerated slightly by the addition of pre-formed cellulose ether to the etherification mixture.[54]

From a Russian laboratory comes a description of the preparation of an allylcellulose (from allyl bromide and alkali-cellulose) of degree of substitution (D.S.) about 2; the allyl cellulose could be separated into an acetone-soluble fraction of D.S. 1·7–1·8 and an ethanol-soluble fraction of D.S. about 2·2. Heating in air, exposure to ultra-violet radiation and the action of benzoyl peroxide, evidently produced some addition-polymerization, and dry chlorine gave a tetra-chloro-derivative soluble in chloroform and tetrachloroethane.[55] T. Timell has described triallyl cellulose as fairly stable, and insoluble in all the common solvents.[56] The same author has prepared various branched-chain ethers of cellulose (*iso*propyl, *sec.*-butyl, *iso*butyl and *iso*amyl) all of D.S. less than 1. These ethers are unlikely to be of any importance for manufacture of plastics, but the method of production is of interest in that etherification, which failed when attempted on alkali-cellulose (presumably owing to the bulky nature of the alkyl groups) was successful when applied to cellulose dissolved in a quaternary ammonium base.[57]

An interesting development is the production from viscose and acrylonitrile of acetone-soluble, water-resistant fibre-forming cyanoethyl ethers of cellulose of high softening point.[58] Cellulose derivatives containing amino groups have been made from alkali-cellulose and 2-aminoethylsulphuric acid.[59] The combined nitration and oxidation of cellulose to form a substantially undegraded ester-acid has been described.[60]

Solvents and plasticizers for cellulose derivatives

H. M. Spurling has reviewed the whole field of current theory on polymer–solvent interaction, emphasizing the importance of parity of cohesive energy density between polymer and solvent, and, especially in polar polymers such as the cellulose derivatives, of solvation and of ionic linkages.[26] The main value of such a review to the worker in this field is in providing ideas, for instance as to the constitution required in a compound if it is to serve as solvent or plasticizer for a particular cellulose derivative; the possibility of actual prediction appears far remote. There is indeed a grave lack in the literature of the data necessary to apply to new problems some of the theories outlined. Cohesive energy densities, for instance (or the data from which they may be calculated) are available in respect of only a small proportion of the solvents and plasticizers known.[61]

K. Thinius has investigated, in connexion with cellulose nitrate and some organic esters of cellulose, the formation of binary solvents both components of which are non-solvents, including mixtures in which one

component is a plasticizer, and the effect of incorporating various condensation polymers in such binary mixtures and in non-solvent binary mixtures (which were in some cases converted in this way into solvent mixtures). The extensive experimental data obtained supported some useful generalizations.[62] Fresh light has been shed on the vexed question of whether acetone forms a definite compound with cellulose nitrate, by determining the absorption-isotherms for vapour-phase and liquid-phase absorption. These showed no evidence of compound-formation.[63] Some interesting information as to the mode of penetration of various solvents into oriented cellulose acetate film has been obtained by watching the process under the microscope.[64] Of interest in connexion with the mechanism of solvation is a Belgian investigation of the hydration of cellulose and its derivatives in which it was found possible to distinguish between hydration of free and of bound (presumably hydrogen-bonded) hydroxyl groups.[65] The effect of dissolved cellulose esters on selective evaporation of the components of binary solvents has been studied.[66] By determination of the solubility of cellulose nitrate fractions of different degrees of polymerization (D.P.) but the same nitrogen content, a linear equation connecting solubility with log D.P. has been obtained.[67] Co-acervation has been studied with reference *inter alia* to cellulose acetate.[68]

Some further attempts have been made on the old problem of providing a plasticizer for cellulose triacetate. One proposal takes advantage of the solvating effect of groups containing a hydrogen atom rendered mobile by adjacent chlorine (as in chloroform) by condensing chloral with pentaerythritol to make the monoacetal and esterifying the product, for instance to form the diacetate.[69] Another plasticizer alleged to be suitable for the triacetate, as well as for other cellulose esters and ethers and for vinyl polymers, is the triacetate of pentane-1 : 2 : 5-triol which is readily obtainable from furfuraldehyde.[70] The possibility that acidity may develop in plasticizers containing ester groups (i.e. most plasticizers for cellulose esters) is a danger that it has been proposed to avoid by the use of nitrophenyl ethers of polyglycols, which are stated to have good compatibility *inter alia* with cellulose acetate.[71] The stability alleged is curious since both ether groups and nitrate groups are often associated with instability.[72] Other monomeric plasticizers proposed for cellulose acetate are : nitrilo-triacetates,[73] higher dialkyl esters of phosphoric acid[74] and aryl phosphoric esters halogenated in the *meta*- or *para*-positions.[75] For cellulose nitrate, polyalkylene mixed esters of capric and caprylic acids have been described as giving high flexibility.[76]

Few polymeric plasticizers for cellulose acetate have yet been described. Among these are condensation polymers of glycols with higher-alkyl-substituted malonic acids.[77] By condensing an alkyl chlorocarbonate with a hydroxy-fatty-acid ester of an alcohol (with elimination of hydrogen chloride) α-carbalkoxy-carbonic esters of the alcohol, which are plasticizers for cellulose esters and ethers, are obtainable ; if allyl alcohol is used the plasticizers can be cross-linked or copolymerized, e.g. with methacrylic esters.[78] It has also been proposed to plasticize cellulose esters and ethers with polyglycol esters of unsaturated polymerizable aliphatic acids, and to cross-link the plasticizer.[79]

The current 'Modern Plastics Encyclopedia' now lists about 200 solvents and nearly as many plasticizers which are on the market in U.S.A. Of the solvents probably about 30 are solvents for ripened cellulose acetates, about 50 for cellulose nitrate, and about 120 for ethyl cellulose. Of the plasticizers, about half the number have useful compatibility with such cellulose acetates and most of them are compatible with ethyl cellulose. Many important properties of these solvents and plasticizers are listed in convenient tabular form, but information on solvent action is missing for many solvents, is sometimes erroneous (as when carbon tetrachloride is listed as a solvent for cellulose acetate) and, like much of the information regarding solvent action in text-books and other literature, is defective in specifying neither the characteristics of the cellulose derivative tested (especially degree of substitution) nor the method of test.[80] More useful information on solvent action can be obtained from some older sources, for instance from W. Coltof's 'Acetate Silk'[81] and from the excellent pamphlets of Hercules Powder Co. on cellulose acetate and ethyl cellulose. With regard to improvements in the commercial grades of old plasticizers, mention may be made of a purer grade of trichloroethyl phosphate[82] (which combines flame-resistance with excellent compatibility with cellulose acetate) and of the increasing availability of tricresyl phosphate free from the toxic *ortho*-isomer.

Manufacture, use and properties of cellulosic plastics

Methods of compounding and working cellulosic plastics without the use of volatile solvents are on the increase, and appear destined eventually to supersede solvent methods entirely, except perhaps in the manufacture of thin films and of celluloid. One development along these lines is the incorporation of the plasticizer and other required ingredients with the cellulose derivative, during passage through a screw-extruder. A machine is now on the market, in which the initial cold-mixing necessary if a homogeneous product is to be obtained, and the final hot-mixing, are effected by intermeshing screws in successive zones; the material is extruded from a third zone, the shape and dimensions of the screws and the passage being adapted to give the pressures necessary in the various zones, and much of the heat required being generated mechanically by the action of the screws.[83] Various systems of intermeshing screws designed to prolong the path of the plastic during homogenization and to prevent its sticking to the sides, have been developed.[84]

The normal hot-extrusion methods of fabricating cellulose derivatives do not give products of accurately predeterminable size owing to a slight variable expansion occurring as the product leaves the die. In a patented method for overcoming this difficulty the die aperture is elongated considerably (e.g. up to 10 ft.), the material is cooled to below its softening point during its passage through the die, and lubricant is supplied to prevent the product sticking in the die.[85] A more recent proposal deals with the sticking tendency by using a split die with reciprocating halves.[86] For extruding tubing, a die has been devised with rotating central and annular members.[87] In making flat, thin-walled tubing by hot-extrusion, inflation by air to a predetermined diameter before cooling has been described.[88] A novel method of making thick sheets on conventional

hot-extrusion machines comprises extrusion through a spiral slot, followed by flattening the extruded material.[89]

With the demand for injection-mouldings of increasing size the supply of the necessary clamping pressure becomes more difficult. In one machine designed to deal with this problem, any slight movement apart of the mould-halves automatically decreases the injection pressure.[90] Restriction of the gate through which the material is injected into the mould to a 'pin-hole' about 0·17 in. in diameter has been found to give improved flow and homogeneity.[91] Great economy in floor-space, and cost, primarily owing to the low clamping-pressure needed, is obtainable with a machine in which the material is injected into an intermediate chamber from which it is transferred through sprue-runners into the mould.[92]

By investigating creep in filaments of plasticized cellulose acetate, G. M. Moelter and E. Schweizer have arrived at the simple relation: $t_1 = te^{-km}$, where t_1 and t are the softening temperatures of plasticized and unplasticized cellulose acetate, m is molar concentration of plasticizer and k is a constant for the plasticizer.[93] As t and t_1 must be expressed in ° C. the theoretical significance of the equation is less obvious than its utility. By pressing together at various temperatures and pressures two discs of the same plastic and determining the force necessary subsequently to separate them, 'critical coalescence temperatures' have been found for, *inter alia*, cellulose acetate and ethyl cellulose, below which little cohesion was brought about even at pressures as high as 10,000 lb./sq. in. These temperatures were related in each case to a transition-point shown by a discontinuity in the density–temperature curve of the polymer. They were reduced by decrease in molecular weight and the addition of solvents and plasticizers.[94]

In film-casting by the evaporative method, addition of a small proportion of a tri-(higher-alkyl) phosphate to the normal casting solution has been found to facilitate stripping.[95] As a film-casting under-layer, for instance for casting cellulose acetate films, sodium cellulose glycollate has been proposed.[96]

Long-chain derivatives of biguanide, and guanidium salts of higher fatty acids, have been suggested for anti-static finishes for films.[97] For packaging foil, an electrolyte which is preferably the salt of an alkyl acid-sulphate and an aliphatic amine, applied together with a water-soluble polyvinyl compound, has been found useful for the same purpose.[98] The incorporation in cellulose-derivative packaging materials of various substances that absorb ultra-violet radiation has been proposed.[99] The extent to which various cellulose derivatives and plasticizers used in packaging support the growth of fungi has been investigated.[100]

Among heat-stabilizers recently proposed for cellulose ether moulding compositions are sulphur dioxide and various simple and polymeric organic sulphites and unstable sulphones, especially in conjunction with a phenylol-substituted terpine.[101,102] A well-planned investigation of the thermal degradation of cellulose ethers by F. McBurney has shown this to be a chain reaction involving transitory formation of peroxides; this reaction is not dependent for velocity on initial degree of substitution

or viscosity, is inhibited by secondary aromatic amines and phenols, and retarded by mercaptans and thio-phenols; the kinetics of it suggest a free-radical mechanism.[103] A similar investigation on cellulose acetate showed up the far greater heat-stability of this material, oxidation occurring only after 160 hours at 145° C., or 12 hours at 160° C.; the factors affecting stability were difficult to determine, apart from the catalytic effect of sulphuric acid.[104] With certain plasticizers, however, e.g. triphenyl phosphate (possibly owing to the development of acidity) heat-stabilizers can be used with advantage even in cellulose acetate compositions, and for this purpose calcium lactate and other alkaline-earth salts of hydroxy-fatty acids have been recommended.[105] The degradation of ethyl cellulose brought about by ultra-violet radiation has been found to have substantially the same mechanism as the heat degradation referred to above.[106] Among light-stabilizers proposed are benzyl benzoate[107] and a wood rosin derivative, $C_{20}H_{22}O_7$, containing phenolic, alcoholic and lactone groups.[108] The results of outdoor exposure of cellulose acetate and ethyl cellulose sheets for 11 months at Miami and 29 at Dayton, Ohio, are now available. They show that little change in appearance occurs but there is a decrease in impact strength of the cellulose acetate (possibly due to loss of plasticizer); there is no correlation with the effect of immersion for 24 hours in water.[109]

The recently developed flame-resistant cellulose acetate plastics (high-acetyl cellulose acetates with a flame-resistant plasticizer) have been discussed in relation to moulding conditions and properties obtainable.[110] From compositions containing ethyl cellulose and a major proportion of a silicone polymer, highly heat-resistant electrical insulating materials, e.g. films, can be obtained.[111] A combination of high dielectric strength with toughness is said to be obtainable from a composition containing ethyl cellulose and polystyrene, plasticized with styrene derivatives.[112] The compatibility of ethyl cellulose with natural and synthetic rubbers is taken advantage of in various compositions to obtain a combination of properties.[113,114] In such compositions the rubber can of course be cross-linked by vulcanization. The problem of cross-linking cellulose derivatives without too great a sacrifice of toughness has as usual invited some further attempts at solution. Partial dechlorination products of chlorinated furfuraldehyde have been proposed as cross-linking agents.[115] The formation of disulphide links by further esterifying cellulose acetate with chloracetic acid or *p*-toluenesulphonyl chloride, and reacting with sodium thiosulphate, thiourea or hydrogen sulphide has been described.[116] Organo-aluminium compounds have also been proposed.[117] For cellulose nitrate, titanium tetrachloride and titanium tetraethyl have been used for cross-linking in a rheological investigation.[118] Cross-linking of cellulose nitrate and acetate by various chlorides and oxychlorides of non-metals has been investigated.[119] It has been proposed to provide cellulose ester optical components with an optically flat, scratch-resistant surface, by coating with a partly condensed amino-plastic and hardening this during a final moulding operation.[120]

C. J. Malm and co-workers have described the development of strippable hot-melt coating compositions based on a cellulose acetate–butyrate

containing 2·4 butyryl and 0·5 acetyl groups; they have given much useful information as to methods of test, and effect of various ingredients.[121] Compositions based on cellulose butyrates or acetate–butyrates of high butyryl content have been described for melt-mould-casting.[122] Cellulose acetate lacquers have been found very suitable as masking agents in dip-coating electrical components with a varnish that, after baking, is to be removed in certain areas.[123] Ethyl cellulose is now being manufactured in Great Britain for melt-coating applications.

A British Standards specification for cellulose acetate moulding materials has been published,[124] and so has an A.S.T.M. tentative standard.[125] Tentative standards have also been published in respect of tests for blocking of plastic sheets, flow-properties of thermoplastic materials, bond-strength of plastics, stiffness, deformation under specific gravity, and Rockwell hardness.[125] New test-methods (and in some cases results of the tests) have also been published in respect of impact strength,[126] abrasion resistance,[127] hardness,[128] weight-loss on heating,[129] and water-vapour transmission and absorption.[130] The determination of molecular weight distribution in cellulose derivatives by fractional absorption (e.g. in charcoal) and fractional extraction has been described.[131,132] A colorimetric method of estimating cellulose nitrate in admixture with other cellulose esters (using diphenylamine) has been described.[133]

Protein plastics

The hardening of protein plastics by formaldehyde after-treatment has obvious disadvantages which it has been sought to avoid by using as internal hardening agents various compounds containing loosely-bound formaldehyde. These have hitherto been unsuccessful owing to premature liberation of formaldehyde. A new series of internal hardening agents, the methylolmelamines, are said to be free from this disadvantage.[134]

In a research directed to obtaining soya bean protein of improved colour, L. L. McKinney and W. F. Sollars have bleached alcohol-extracted and hexane-extracted soya-bean meal with sulphurous acid. The meal obtained was of a light tan colour owing evidently to natural pigments in the meal.[135]

Various cheap sources of protein, which might find limited use in plastics have been investigated. Thus it has been proposed to obtain protein suitable for moulding by heating keratin-containing waste material with aqueous alcohol and then precipitating the protein.[136] Another method described for recovering keratin (for instance from wool-waste) includes solution in alkaline thio-glycerol.[137] The composition, structure and physiochemical properties of horn-keratin have been investigated.[138,139]

A review of the importance of various constitutional factors of protein in the production of protein fibres, by S. R. Hoover and co-workers, is of interest in connexion with the manufacture of protein plastics, where many of the same factors are also important. Besides the physical properties of the proteins, their reactions with formaldehyde are reviewed

and determination of chain length, which is relatively low compared with that of other fibre-forming polymers, is described.[140]

References

[1] *Mod. Plastics*, 1948, **26** (2), 154 ; 1949, **27** (2), 142
[2] Haas, H., *Makromol. Chemie*, 1948, **2**, 217
[3] *Chem. Abs.*, 1949, **43**, 1969, 1970, 1971
[4] Ibid., 1970
[5] Ibid., 1968
[6] Ibid., 1973
[7] Wiggins, L. F., *Chem. & Ind.*, **1949**, 555
[8] Delga, J., *Mem. Serv. Chim. Etat*, 1947, **33**, 7
[9] Monthly Digest of Statistics, 1949, **45**, 46
[10] Prevot, A. R. and Raynaud, M., Fr. Pat. 947,977
[11] Richter, J. C. F. C., U.S.P. 2,474,862
[12] Gans, L. R., B.P. 625,130
[13] Callahan, J. R., *Chem. Engng.*, 1949, **56**, 137
[14] Pearl, J. A., *Chem. Engng. News*, 1948, **26**, 2950
[15] Grant, Julius, Lecture to the Society of Chemical Industry, Oct. 3, 1949
[16] Herrent, P. and Govaerts, R., *J. Polymer Sci.*, 1949, **4**, 289
[17] Alexander, W. J. and Mitchell, R. L., *Chem. Engng. News*, 1949, **27**, 1130
[18] Brabender, G. J., Baird, J. W. and Daily, J. M., U.S.P. 2,466,633
[19] Tatomer, H. N. and Mathieson Alkali Works, B.P. 625,201
[20] Palestine Potash Ltd., B.P. 615,604
[21] Martin, M. E., Umansky, M. and Celanese Corpn. of America, U.S.P. 2,482,858
[22] Chedin, J., *Chim. et Industr.*, 1949, **61**, 571 ; Chedin, J. and Tribt, A., *Mem. Serv. chim. Etat* ,1947, **33**, 143
[23] Richter, G. A., Maclaren, R. A. and Eastman Kodak Co., U.S.P. 2,487,892
[24] Hincke, W. B., Malcolm, C. J. and Eastman Kodak Co., U.S.P. 2,478,396
[25] *Chem. Engng. News*, 1949, **27**, 2906
[26] Spurling, H. M., *J. Polymer Sci.*, 1948, **3**, 714
[27] British Celanese Ltd., B.P. 616,033
[28] Richter, G. A. and Eastman Kodak Co., U.S. Patent Application Serial No. 667,105
[29] Stratveit, N. N. and Schie, A. J., B.P. 615,817
[30] Bourne, E. J., Stacey, M., Tatlow, J. C. and Tedder, J. M., *J. chem. Soc.*, **1949**, 2976
[31] Hamalainen, C. and Reid, J. D., *Ind. Eng. Chem.*, 1949, **41**, 1018
[32] *Chem. Abs.*, 1949, **43**, 2769
[33] Atkins, W. G. and Callow, H. J., B.P. 615,132
[34] Fordyce, R. and Crane, C. L., U.S.P. 2,478,383 ; Richter, G. A., Herdle, L. E. and Eastman Kodak Co., U.S.P. 2,478,425
[35] Rhodiaseta, B.P. 628,844
[36] Dreyfus, C., Rowley, R. D. and Thomson, R. F., U.S.P. 2,456,688 ; British Celanese Ltd., B.P. 627,861
[37] Malm, C. J., Crane, C. L. and Eastman Kodak Co., U.S.P. 2,469,395
[38] Rowley, R. D. and Celanese Corpn. of America, U.S.P. 2,475,678 ; British Celanese Ltd., B.P. 616,132
[39] Seymour, G. W., White, B., Bellucci, A. J. and Celanese Corpn. of America, U.S.P. 2,470,191–2
[40] British Celanese Ltd., B.P. 630,388
[41] Idem, B.P. 630,937
[42] Idem, B.P. 620,726
[43] Rosen, L. J. and Celanese Corpn. of America, U.S.P. 2,490,164
[44] British Celanese Ltd., B.P. 611,665
[45] Malm, C. J. and Smith, H. L., *Ind. Eng. Chem.*, 1949, **41**, 2325
[46] Gavaert Photo-Production N.V., B.P. 615,602
[47] Martin, M. E., Reed, L. G., Thomas, J. L. and Celanese Corpn. of America, U.S.P. 2,484,108 ; *see* also Fox, H., U.S.P. 2,482,142-3 ; Fox, H., Kneisley, J. W. and Hercules Powder Co., U.S.P. 2,489,128
[48] Entwistle, D. *et al.*, *Textile Res. J.*, 1949, **19**, 527, 609

[49] Erickson, D. R., U.S.P. 2,469,764
[50] Klug, E. D. and Hercules Powder Co., B.P. 623,607
[51] Kayser, G. M. A. and American Enka Corpn., U.S.P. 2,473,954
[52] Myers, W. H. and Hercules Powder Co., U.S.P. 2,482,862
[53] Cyrot, J. *et al.*, *Mem. Serv. Chim. Etat.*, 1947, **33**, 159, 169
[54] Finlayson, A. S. and Hercules Powder Co., U.S.P. 2,482,862
[55] *Chem. Abs.*, 1949, **43**, 5943
[56] Timell, T., *Svensk Papperstidning*, 1949, **52**, 165
[57] Timell, T. *Svensk kem. Tidskr.*, 1949, **61**, 49
[58] MacGregor, J. H. and Courtaulds Ltd., B.P. 605,357
[59] Guthrie, J. D., U.S.P. 2,459,222
[60] Kenyon, W. O., Fowler, W. F. and Eastman Kodak Co., U.S.P. 2,472,591
[61] For some figures *see* *Chem. Rev.*, 1939, **8**, 329; *I.R.I. Trans.*, 1943, **18**, 266; *Trans. Faraday Soc.*, 1946, **42**, 22; *J. Amer. chem. Soc.*, 1949, **71**, 3548
[62] Thinius, K., *Farben, Lacke, u. Anstrichstoffe*, 1948, **2**, 97, 117, 159
[63] Campbell, H. *et al.*, *J. Polymer Sci.*, 1948, **4**, 247
[64] Hartley, G. S., *Trans. Faraday Soc.*, 1949, **45**, 820
[65] Champetier, G. and Clement, P., *Bull. Soc. Chim. Belg.*, 1948, **57**, 236
[66] Fordyce, C. R. and Simonson, D. R., *Ind. Eng. Chem.*, 1949, **41**, 104
[67] Scherer, P. C. and Masuelli, F. J., *Rayon synth. Text.*, 1949, **30**, 47
[68] Dervichian, D. G., *Research*, 1949, **2**, 210
[69] Aiken, J. K. and Geigy Co. Ltd., B.P. 629,691
[70] Grunfeld, M., Cottet, E. C. and Société des Usines Chimiques Rhône-Poulenc, U.S.P. 2,476,976
[71] Doelling, G. L. and Adams, K. H., U.S.P. 2,485,712
[72] *See* e.g., Wehr, W., *Kolloidzschr.*, 1939, **88**, 185, 290
[73] Cilag chem. indust. Laboratorium A.G., Swiss Pat. 242,355
[74] Toy, A. D. F., U.S.P., 2,400,577; 2,471,463
[75] British Celanese Ltd., B.P. 628,477
[76] Strauss, F. A., U.S.P. 2,469,446
[77] Floyd, D. E., U.S.P. 2,483,726
[78] Rehberg, C. E., U.S.P. 2,456,264
[79] Stamberger, P., U.S.P. 2,459,298
[80] 'Modern Plastics Encyclopedia,' 1949
[81] Abstracted in *J. Soc. chem. Ind.*, 1937, **56**, 891
[82] 'Flexol 3 C.F.', *Plastics News Letter*, 1949, **9** (41), 4
[83] *Mod. Plastics*, 1949, **26** (10), 87
[84] E.g. S.P.A. Lavorazione Materie Plastiche, B.P. 618,518 and many other patents of the same company
[85] Plax Corpn., B.P. 563,121
[86] Idem, B.P. 620,333
[87] Cozzo, G. and Hydropress Inc., U.S.P. 2,461,630
[88] Fuller, E. D. and Visking Corpn., U.S.P. 2,461,975
[89] S.P.A. Lavorazione Materie Plastiche, B.P. 628,467
[90] Lester Engineering Co., B.P. 631,641
[91] Barnett, L. H., *India Rubb. World.*, 1949, **120**, 340
[92] *Mod. Plastics*, 1949, **26** (11), 68
[93] Moelter, G. M. and Schweizer, E., *Ind. Eng. Chem.*, 1949, **41**, 684
[94] Meissmer, H. P. and Merrill, E. W., *Mod. Plastics*, 1949, **26** (8), 104
[95] Easton, R. P. and General Aniline and Film Corpn., U.S.P. 2,464,784
[96] Photo-Products Gavaert, S.A., F.P. 919,736
[97] General Aniline and Film Corpn., B.P. 623,061 and 625,870
[98] Daly, A. J., Hawtin, P. R. and British Celanese Ltd., B.P. 627,027
[99] Riley, E. G. B., B.P. 617,431
[100] Penn, W. S., *British Packer*, 1949, **11** (1), 24, 36
[101] Myles, W. J. and Celanese Corpn. of America, U.S.P. 2,465,914–5
[102] Paist, W. D., Berardinelli, F. and Celanese Corpn. of America, U.S.P. 2,472,227
[103] McBurney, L. F., *Ind. Eng. Chem.*, 1949, **41**, 1251
[104] Evans, F., McBurney, F., ibid., 1260
[105] Santoro, O., Jasko, E. and Celanese Corpn. of America, U.S.P. 2,449,149
[106] Evans, F. and McBurney, F., *Ind. Eng. Chem.*, 1949, **41**, 1256
[107] Hitchens, R. M. and Monsanto Chemical Co., U.S.P. 2,455,581

[108] Cox, R. F. B. and Hercules Powder Co., U.S.P. 2,454,273
[109] Long, J. K., *Brit. Plastics*, 1949, **21**, 619
[110] Bentivoglio, M., *Mod. Plastics*, 1949, **26**, (9), 66
[111] Johannson, O. K. and Corning Glass Works, U.S.P. 2,466,434
[112] Standard Telephones & Cables Ltd., B.P. 629,469
[113] Harvey, M. T. and Harvel Research Corpn., U.S.P. 2,485,597–8
[114] Gidley, P. T., U.S.P. 2,462,629
[115] Novotny, E. E. and Vogelsang, G. K., U.S.P. 2,475,801
[116] Izard, E. F. and Morgan, P. W., *Ind. Eng. Chem.*, 1949, **41**, 617
[117] Jullander, E. I., Swedish Pat. 120,451 ; *Chem. Abs.*, 1948, **42**, 7528
[118] Jullander, I. and Blom-Sallin, B.-S., *J. Polymer Sci.*, 1948, **3**, 804
[119] Urbanski, T., *Bull. Soc. Chim. Belg.*, 1948, **57**, 467
[120] Barnes, A. and Polaroid Corpn., U.S.P. 2,481,809
[121] Malm, C. J., Nelson, H. B. and Hiatt, G. D., *Ind. Eng. Chem.*, 1949, **41**, 1065
[122] Salo, M., Vivian, H. F. and Eastman Kodak Co., U.S.P. 2,481,687
[123] White, R. W. and Westinghouse Electric Corpn., U.S.P. 2,476,937
[124] B.S. 1524 : 1949
[125] A. S. T. M. Standards, 1948, Supplement III B
[126] Quackenbos, H. M. *et al.*, *A.S.T.M. Bull.*, 1949, No. 159, 56
[127] Schiefer, H. F., *et al.*, ibid., 73
[128] Hoekstra, J., Nijveld, H. A. W., *Rec. Trav. chim. Pays. Bas.*, 1948, **67**, 685
[129] Marks, M. E., *A.S.T.M. Bull.*, 1949, No. 159, 53
[130] Kovces, J., *Chim. Phys.*, 1948, **45**, 258
[131] Claesson, S., *Chem. & Ind.*, **1949**, 12
[132] Desneux, V., *Bull. Soc. Chim. Belg.*, 1948, **57**, 416
[133] Roberts, A. G., *Analyt. Chem.*, 1949, **21**, 813
[134] Pinner, S. H. and B.X. Plastics Ltd., B.P. 630,150
[135] McKinney, L. L., Sollaro, W. F., *Ind. Eng. Chem.*, 1949, **41**, 1058
[136] Ward, W. H. and Binkley, C. H., U.S.P. 2,474,339
[137] Evans, R. L., U.S.P. 2,434,688
[138] Bandyopadhyay, N., *J. Indian chem. Soc., Industr. News Ed.*, 1948, **11**, 148
[139] Rao, A. J., *J. sci. industr. Res. India*, 1948, **7B**, 124
[140] Hoover, S. R., Kokes, E. L. and Peterson, R. F., *Text. Res. J.*, 1948, **18**, 423

RESINS, DRYING OILS, VARNISHES AND PAINTS

BY MEMBERS OF THE OIL AND COLOUR CHEMISTS' ASSOCIATION

NATURAL AND SYNTHETIC RESINS (R. S. Robinson, F.R.I.C., A.R.T.C.S., A.P.I.)

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EXAMINATION of articles in the technical press and of British and American patent literature appearing during 1949 has shown that there has been a considerable increase in the employment of resins of ethenoid origin in the surface-coating industry. There has also been a renewed interest in synthetic resins for the formulation of water paints, and since one of the best methods of introducing a resin into such a paint is by means of a pre-formed emulsion, latices obtained directly by the emulsion-copolymerization technique from vinyl compounds such as vinyl chloride, vinylidene chloride, styrene (and butadiene), vinyl acetate and acrylic derivatives are attracting a great deal of attention in this field. Another noticeable feature is the decrease in the amount of published work on hard varnish resins, both of natural and synthetic origin. This might be taken as some confirmation of the belief that the orthodox oil varnishes are rapidly being replaced by other media. A contributory factor to this trend is probably the world vegetable-oil shortage, since such oleo-resinous products as oil-modified alkyds and styrene copolymers require a much lower proportion of oil than the older stand-oil varnishes. Such properties as durability, gloss retention, etc. have no doubt also been considered. Regarding durability, J. S. Long[1] has described work carried out on the absorption and transmission of ultra-violet light by dried films of various oils and resins. He has stated that vehicles of known good durability show high transmission and considers that from his results the correlation between ultra-violet light absorption and exterior durability characteristics of a film appears to be established. The employment of maleic anhydride in the manufacture of synthetic resins, mainly alkyds, is still on the increase: its annual production in the U.S.A., chiefly from vapour-phase oxidation of benzene (and to a small extent from recovery from phthalic anhydride manufacture) has now exceeded 12 million lb.[2]

On the question of molecular weight distribution and the separation of products into fractions having different average molecular weight ranges, an American patent[3] describes a process in which a solution of the resin in a saturated hydrocarbon solvent is passed through a bed of silica gel. This rapid adsorption process substantially removes those polymers having the lower average molecular weights.

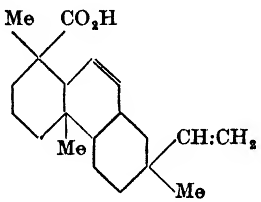
Various methods of determining olefinic unsaturation have been suggested and some in current use depend upon bromine addition. One of the chief disadvantages of such methods, however, is the ease with

which bromine reacts by substitution as well as by addition ; it is therefore necessary to take very careful precautions in respect of time and temperature. A method has been described by A. M. Caccia-Bava,[4] however, which he claims is almost free from risks arising from excessive standing before completion of the determination. The method employs dibromopyridine acetate, and results are said to vary only 1·6% if the determinations are left standing for as long as a fortnight before completion.

Natural resins and simple derivatives

Investigations on Congo copal have been continued and D. A. Sutton[5] working in this country has found that it consists of a mixture far more complex than has hitherto been reported. The components vary from simple sesquiterpenes to polycarboxylic acids of extremely high molecular weights ; his results appear to bring new light on the reactions that take place during running of the resin. J. Schreiber[6] regards the running of copal as a type of equilibrium between formation and decomposition of esters resulting in a greater uniformity in the sizes and complexity of the molecules.

Rosin is still one of the cheapest and most widely used natural resins ; it is therefore to be expected that new methods of 'modifying' it and new results of work on its constitution should continually be described. The structure of the abietic acid component has been established now for some considerable time but that of pimaric acid has been disputed. G. C. Harris and T. F. Sanderson[7] claim that they have now confirmed the correctness of the formula:



G. A. Vassilier[8] working mainly with French rosin has examined the stages through which rosin passes during strong heating. He has found that there are five reasonably well defined stages : (i) dehydration, resulting in (ii) molecular rearrangement, (iii) loss of carbon dioxide, (iv) loss of some carbon monoxide and finally (v) hydrogen migration causing polymerization. Most of the volatile products are evolved during stage (ii).

One of the troubles encountered with zinc resinates has been instability to a greater or lesser degree in solution. Newport Industries, Inc.[9] claim in a patent that products which are perfectly stable in solution result from the thermal reaction between a partially polymerized rosin and approximately 5% of zinc oxide in the presence of a low molecular-weight carboxylic acid such as acetic, or a salt capable of liberating such an acid when heated with the rosin. Another 'modified' rosin which has been described is that made by reacting the rosin with the resinous

intermediate prepared from acetone and formaldehyde, claimed by F. H. Levey and Co.[10]

A. Wright[11] has tabulated a number of colour tests for the identification of various resins with particular attention to shellac. Another method of identifying a resin by a colour reaction is that for dehydroabietic acid described by W. Sandermann[12]: this method comprises the sulphonation of a sample in the cold, followed by neutralization with sodium hydroxide; the blue–violet colour which develops varies with the amount of dehydroabietic acid in the sample.

Water-insoluble coatings from casein have been made by Ciba Ltd.[13] by peptizing the casein with a little urea and then reacting the resultant colloid with formaldehyde. Other protective finishes derived from proteins are the chromated protein coatings which have recently been described.[14] In addition to their acting as binding media they are also good corrosion inhibitors and are resistant to bacteria.

Two derivatives of natural rubber, applications for which appear to be steadily increasing in the paint and varnish industry, are cyclized rubber and chlorinated rubber. Both of these, particularly chlorinated rubber, the properties of which have been reviewed by B. S. Gidvani,[15] are being employed where coatings having both good chemical resistance and appearance are required. They form useful bases on which to formulate coatings for use on concrete, plaster, etc. Chlorinated rubber has the added advantage of being non-inflammable.

Phenolic and amino-formaldehyde resins

On the preparation of pure oil-soluble phenolics, Sherwin-Williams Co.[16] have claimed in America a process for effecting uniform and homogeneous reaction between a water-insoluble phenol such as *p*-phenylphenol and aqueous formaldehyde under acid conditions by incorporating a solvent for the phenol such as xylol and a surface-active agent. H. L. Allen and E. G. Kerr[17] have prepared a series of modified phenol–formaldehyde resins by reacting a polymerizable compound such as styrene with a phenol, maleic anhydride and formaldehyde. A great deal of work has been done in past years in America on the use of furyl compounds in synthetic resins and particularly in conjunction with phenol–formaldehyde types. Two patents have recently been granted to Government workers in this country describing such use of furfuraldehyde. In one of these L. N. Phillips[18] claims that the incorporation of 5% of furfuraldehyde and an equal amount of furfuryl alcohol will produce cold-setting phenol–formaldehyde resins; in the other, J. E. Lennard-Jones and co-workers[19] state that they have found that in order to make satisfactory resins of the fural-modified phenol–formaldehyde type, the proportion of phenol to the furfuraldehyde, formaldehyde and catalyst must be maintained between very restricted limits: these limits are quoted.

Discussing the hardening of phenol–aldehyde resins, E. G. K. Pritchett[20] has suggested that the cured mass consists not of a cross-linked structure but of molecules having continually branching chains something like trees with branches, and that these branches intertwine with branches of other molecules; being rigid, they cannot be disentangled by solvents or by heat.

In the field of amino-resins, W. Nebel[21] has described a nitrocellulose-compatible urea resin made by condensing urea with a pre-formed condensate of a ketone such as methyl ethyl ketone and formaldehyde. Resinous Products and Chemical Co.[22] have claimed the preparation of a series of modified urea–formaldehyde resins of special value in the manufacture of high wet-strength papers ; these resins employ guanidine as the specific modifying agent. Another use for guanidine (or, rather, certain of its derivatives) is that of latent catalysis for amino-resins. D. A. Nagy[44] has described how acyl carbamylguanidine compounds can be used as catalysts for the thermal curing of amino-formaldehyde resins whilst having no reactivity whatsoever at storage temperatures. These compounds are stated to be relatively inexpensive compared with other latent catalysts which have been suggested.

Much (mainly patents) has been published on melamine, particularly in connexion with its manufacture. In two such patent specifications, Du Pont de Nemours Co. claim that the gases obtained by the thermal decomposition of urea are catalytic in the preparation of melamine from urea,[23] and that the yield can be improved by heating a urea pyrolysate with water under conditions of high temperature and pressure.[24] During the manufacture of melamine in vessels of various stainless steel alloys, the American Cyanamide Co.[25] observed unusual corrosion phenomena. Very slight differences in the composition of the steel alloys resulted in widely different corrosion characteristics. The most important observation made by them was that all the alloys used corroded very badly if the reaction mixture were to contain more than about 50–100 p.p.m. dissolved iron. The introduction of more than this quantity of iron into the system from the vessel during the initial stages of the reaction can be prevented by the incorporation of minute quantities of chromates or phosphates.

Alkyd resins

Recent advances and trends in alkyd resins have been reviewed by T. H. G. Michael.[26] He describes how manufacturing plant design is changing : the modern preference is for Dowtherm or fused-salt heating of the kettles and the recently developed solution method of preparation, in which water is removed azeotropically, helping to produce much paler colours ; in addition, progress is being made with vinyl-modified alkyds. There is at present a great deal of interest in styrenated alkyds.

The American synthetic resin industry has now an additional source of glycerol : its commercial synthesis from propylene obtained by the cracking of petroleum.[27] A new synthetic polyhydric alcohol described in the U.S.A. is the pentahydric 2 : 2 : 6 : 6-tetramethylol*cyclo*hexanol[28] obtained by the condensation of *cyclo*hexanone with formaldehyde in the presence of lime. Its use as the polyhydric-alcohol component of alkyd resins has been stated to produce improved solubility and compatibility ; the drying properties, film hardness, etc. usually associated with alkyds made from alcohols having several primary alcohol groups in a symmetrical molecule are also said to be developed. As regards alcoholysis of oils, J. Petit[29] has described work on reactions which occur when glycerol is

heated with linseed oil as in the preparation of the so-called 'monoglyceride.' In addition to an equilibrium being set up between mono-, di-, and tri-esters, there are several side reactions that occur, the chief of which is the inter-etherification of glycerol molecules. Under the conditions normally employed for the alcoholysis process no polymerization of the oil takes place through its unsaturated fatty chains.

One of the earliest difficulties experienced in the use of maleic anhydride in alkyds was that of obtaining completely homogeneous products when employing it as the sole polybasic acid component of oil-modified types, particularly when starting with vegetable-oil fatty acids. C. G. Moore[30] has recently stated that this can be done by heating the fatty acids with an equimolecular proportion of glycerol until the esterification is approximately 60% complete, before adding the maleic anhydride. It is also claimed that this method results in products of considerably lower acid value than the conventional monoglyceride process. Troubles with complete homogeneity and turbidity similar to those experienced earlier when using maleic anhydride were also encountered when efforts were made recently to employ terephthalic acid; this acid has aroused much interest in the last few years as its glycol polyesters constitute Terylene, the new synthetic filament. It has now been found, however, by D. Atherton and J. K. Lovell[31] that if terephthalic acid is used in the form of a lower alkyl ester perfectly satisfactory alkyd resins can be obtained.

Another dicarboxylic acid of value in alkyd resin manufacture is sebacic acid. There was some interest in this acid before the war and it was found that P.V.C. compositions plasticized with sebacate resins retained their flexibility at very low temperatures, and were thus of particular value for use in equipment required to withstand high-altitude or arctic conditions. However, the tremendous rise in the price of castor oil, from which this acid is derived, limited its usage; but now that the price of the oil has fallen it is likely that there will be renewed interest in its employment. H. Jones and J. K. Aiken[32] have pointed out that the optimum use of sebacic acid is in plasticizing non-drying resins, especially for use in urea and nitrocellulose finishes; they also describe how a partial replacement of phthalic anhydride by sebacic acid in drying-oil-modified alkyd resins effects greatly improved flexibility without any undue sacrifice of other physical properties.

Probably the most important development in alkyd resins is in the copolymer field. The copolymers of styrene and drying-oil-modified alkyd resins have been found to air-dry or stove in abnormally short times and to produce films of high water-resistance and good colour-retention. There has also been increased employment of alkyd resins, generally of the unmodified unsaturated class, in 'contact' resins where copolymerization with vinyl compounds is effected *in situ*.

J. B. Martin,[33] in a paper on chlorinated rubber, has stated that alkyd resin finishes modified with about 25% of this material have not only much improved resistance to chemical attack but also increased rate of drying and greater hardness.

A continuous process suitable for the preparation of alkyd resins has been described by E. Sunderland and C. W. Andrews.[34] This process involves flow down a column somewhat similar to a packed fractionating

column; it depends on the fact that the reaction mixture is spread as a moving film of extremely large area over the surfaces of the packings. The column is heated and an upward current of inert gas removes the liberated water of esterification as it is produced.

Analysis.—Two new methods for the identification of the dicarboxylic acid components of alkyd resins have been described in American literature: one method, due to R. W. Stafford, R. J. Francel and J. F. Shey[35] consists in treating the resin with benzylamine; the dibenzylamides of the acids are produced and these are readily identified by their melting points, nitrogen contents and/or infra-red spectra. The other, which is a systematic procedure and which can be used either qualitatively or quantitatively, has been described by M. H. Swann.[36] The scheme depends largely upon the different solubilities of their lead, zinc, cadmium, mercurous and silver salts.

Ethenoid and associated resins

Of the vinyl compounds capable of being employed in making resins for the surface-coating resins, styrene is undoubtedly the one to which most reference has been made in the literature during the past 12 months. There has been a great deal of investigation work done on the nature of the chemical reactions taking place during the copolymerization of styrene with drying oils; from the conclusions of J. Rinse and C. Korf[37] it would appear that this problem is by no means settled. It is presumed that the reactions between styrene and drying-oil-modified alkyd resins in the preparation of styrenated alkyds, in which interest is growing very rapidly in both Europe and America, are somewhat similar to those occurring when styrene is heated with bodied drying oils. Additional patents have been granted in respect of both the Berger and Dow processes for the preparation of such styrene copolymers. In one of the patents for the Berger process L. E. Wakeford, D. H. Hewitt and F. Armitage[38] claim improvement in the properties of the products by incorporating in the original partially polymerized oil mixture a proportion of a conjugate trienic oil. Increase in the unsaturated reactivity of the reaction system is also the subject of a Dow Chemical Company's patent[39] in which it is claimed that incorporation of a little divinylbenzene overcomes some of the disadvantages previously possessed by their methylstyrene-modified styrene/oil copolymers. They also claim[40] that mechanical properties of styrene copolymers are improved by the replacement of a very small percentage of the styrene by *p*-chlorostyrene. Such uses of substituted styrenes to modify the properties of polymers and copolymers of styrene have also been discussed in some detail by F. W. Reinhart.[41] Another patent of Lewis Berger and Sons Ltd.[42] of particular interest in the styrenated alkyd field is one claiming the process of styrenation of drying oil fatty acids which can afterwards be esterified alone or employed partially or wholly as the oil-modifying constituents of alkyd resins. The Sherwin-Williams Co.[43,45] have prepared styrenated varnishes by the thermal reaction of styrene with a drying oil and an acidic resin, subsequent esterification being carried out if desired. Another modification of the styrene/drying oil class of medium has been described by Resinous Products and Chemical Company[46]

who have chosen *cyclo*pentadiene, another polymerizable material which is likely to become reasonably plentiful. The *cyclo*pentadiene and styrene are first copolymerized together and then later reacted with the oil.

The probability of polystyrene ever being used to any great extent in lacquers is rather remote owing to its relatively poor mechanical properties, but the possible replacement of nitrocellulose in coating compositions by a derivative of polystyrene—nitrostyrene—has been suggested by I.C.I. Ltd.[47] who have satisfactorily nitrated the pre-formed polystyrene. It is claimed that this product is much more acid-stable than nitrocellulose.

As previously reported, there has been a revival in the interest in water paints and it is therefore to be expected that since a large proportion of vinyl polymers and copolymers are prepared by the emulsion process, the resultant latices would attract attention ; the coagulation and isolation of the polymer are unnecessary, and in most cases undesirable, for this type of application. Latices of polyvinyl acetate,[48] polyacrylates[49], polyvinyl and polyvinylidene chlorides, polyvinyl formals[50] and styrene–butadiene copolymers have been examined ; several have already found large-scale application in the formulation of water paints having some oustanding properties. The dry products isolated after the emulsion copolymerization of styrene and butadiene (high styrene content) are in use in the U.S.A. as lacquer resins. The emulsion polymerization of vinyl chloride containing up to 5% of trichlorethylene is said by R. E. Morgan and P. N. Curry[51] to produce a resin which is flexible enough to be used as the base of coating compositions ; at the same time it possesses the high resistance to acids and alkalis normally associated with P.V.C.

The adhesion of films of ethenoid resins, particularly to aluminium, has been investigated by workers in the U.S.A. S. Moses,[52] working with polystyrene, P.V.C. and polymethyl methacrylate, has shown that adhesion depends in all cases on the formation at some stage of a fluid state at the polymer–metal interface. His measurements of adhesion were made by the new technique employing ultrasonic vibrations. The relationship between adhesion, temperature and molecular weight has been deduced by A. D. McLaren and C. J. Seiler[53] who used polyvinyl acetate for illustration. They find that, provided the molecular weight is high enough to prevent cohesive failure, adhesion is independent of molecular weight and that temperature and chemical composition are the important factors.

Miscellaneous

The uses of silicones in the paint and varnish industry are by now well known and the amazing surface-tension effects of certain of these compounds have no doubt been experienced by most chemists in the industry. It is now claimed by The British Thomson-Houston Co., Ltd.[54] that the wetting power of silicones is substantially increased by the use of compounds of the type $Me_3Si(C_6H_4X)$ where X is a halogen atom. The use of such compounds with a halogen attached directly to the aromatic nucleus enables a benzene ring to be introduced between silicon atoms in silicone resins. Vinyl- and allyl-silicone polymers have been described by D. T. Hurd and G. F. Roedel[55] and silicates similarly modified by allyl groups

are the subject of a patent granted to the Pittsburgh Plate Glass Company.[56] Hitherto esters of silicic acid have been prepared by reacting alcohols with silicon tetrachloride, hydrochloric acid being a by-product. The handling and disposal of the large quantities of this hydrochloric acid constitute a difficult problem; in addition silicon tetrachloride is normally quite expensive. The British Thomson-Houston Co. Ltd.,[57] however, have described a method by which aliphatic esters of silicic acid can be obtained at a relatively low cost and without production of any corrosive by-products by the reaction of the appropriate alcohol with magnesium silicide.

G. M. Kline[58] has recently described how polymerized furfuryl alcohol has proved to be a valuable aid against corrosion by acids and alkalis in chemical plants. Their chief failing, however, is lack of flexibility and consequent cracking by vibration, impact or even moderately high ambient temperatures. A preparation of these resins is also claimed by L. N. Phillips[59] who has found that the acid catalyst used in their manufacture must possess a dissociation constant of between $2{\cdot}0 \times 10^{-1}$ and $2{\cdot}0 \times 10^{-4}$ if satisfactory products are to be obtained.

From time to time in the past workers have published results on the preparation of polymers from acenaphthylene. It has been pointed out[60] that this compound is easily obtained from acenaphthene found in coal tar, that it cannot only be self-polymerized but will also copolymerize with such monomers as styrene and methyl methacrylate; it is suggested that resins of value can be obtained from it. The various methods of producing acenaphthylene have in fact been recently reviewed by J. Idris Jones.[61]

During the cracking of petroleum as in the manufacture of motor fuels from heavy naphthas, such as by catalytic aromatization, fractions are obtained which are rich in alkyl naphthalenes. These, when condensed with formaldehyde, have yielded resins which from preliminary tests appear to give excellent results in linseed- and tung-oil varnishes.[62] Hard-varnish resins are also being prepared by the catalytic polymerization of some of the higher-boiling unsaturated fractions obtained from these cracking plants.

Amongst other items of interest to the resin chemist is the copolymerization of *cyclo*pentadiene with drying oils[63] claimed by the Pittsburgh Plate Glass Co. and the pronounced gelling influence of aluminium alcoholates in drying oil compositions described by H. W. Chatfield.[64]

References

1 Long, J. S., *J. Oil Col. Chem. Ass.*, 1949, **32**, 401
2 Skeen, J. R., *Chem. Engng. News*, 1948, **26**, 3684; *Paint Oil Chem. Rev.*, No. 128, 141
3 Sun Oil Co., U.S.P. 2,462,564
4 Caccia-Bava, A. M., *Ateneo parmense*, 1947, **18**, 467; *Paint Oil Chem. Rev.*, No. 131, 420
5 Sutton, D. A., *J. chem. Soc.*, **1949**, 676
6 Scheiber, J., *Farbe u. Lack*, 1948, **54**, 194
7 Harris, G. C. and Sanderson, T. F., *J. Amer. chem. Soc.*, 1948, **70**, 2081
8 Vassilier, E. A., *Bull. Soc. chim. Fr.*, 1947, 1080; *Paint Oil Chem. Rev.*, No. 127, 53
9 Newport Industries, B.P. 612,808
10 F. H. Levey Co., B.P. 625,144

[11] Wright, A., *Oil Col. Tr. J.*, 1949, **115**, 784
[12] Sandermann, W., *Analyt. Chem.*, 1949, **21**, 587
[13] Ciba Ltd., B.P. 627,301
[14] *Prod. Finish.*, 1949, **2**, 54
[15] Gidvani, B. S., *Paint Manuf.*, 1949, **19**, 419
[16] Sherwin-Williams Co., U.S.P. 2,463,501; *Paint Oil Chem. Rev.*, No. **131**, 472
[17] Allied Chemical and Dye Corpn., U.S.P. 2,456,358
[18] Phillips, L.N. and Royal Aircraft Establishment, B.P. 627,717
[19] Lennard-Jones, J. E. *et al.*, Ministry of Supply, B.P. 629,584
[20] Pritchett, E. G. K., *Chem. & Ind.*, **1949**, 295
[21] Du Pont de Nemours & Co., U.S.P. 2,389,682
[22] Resinous Products & Chemical Co., B.P. 613,622
[23] Du Pont de Nemours & Co., B.P. 628,255
[24] Idem., B.P. 628,250
[25] American Cyanamid Co., B.P. 625,890
[26] Michael, T. H. G., *Canad. Chem.*, 1948, **32**, 916
[27] *Chem. Engng. News*, 1948, **26**, 2770
[28] Wittcoff, H., *Oil Col. Tr. J.*, 1949, **116**, 728
[29] Petit, J., *Amer. Paint J.*, 1948, **33**, 82
[30] Glidden Co., U.S.P. 2,461,564; *Paint Oil Chem. Rev.*, No. 129, 240
[31] Atherton, D., Lovell, J. K. and I.C.I. Ltd., B.P. 629,490
[32] Jones, H. and Aiken, J. K., *J. Oil Col. Chem. Ass.*, 1949, **32**, 150
[33] Martin, J. B., *Canad. Chem.*, 1949, **33**, 208
[34] Sunderland, E. and Andrews, C. W., *J. Oil Col. Chem. Ass.*, 1949, **32**, 523
[35] Stafford, R. W., Francel, R. J. and Shay, J. F., *Analyt. Chem.*, 1949, **21**, 1454
[36] Swann, M. H., ibid., 1448
[37] Rinse, J. and Korf, C., Oil Col. Chem. Ass. Rothesay Conference, 1949, Preprint
[38] Wakeford, L. E., Hewitt, D. H., Armitage, F. and Lewis Berger & Sons Ltd., B.P. 609,750
[39] Dow Chemical Co., U.S.P. 2,468,798; *Chem. Abs.*, 1949, **43**, 5639b
[40] Idem., U.S.P. 2,398,736
[41] Reinhart, F. W., *Chem. Industr.*, 1948, **62**, 235
[42] Cottrell, J. A., Hewitt, D. H. and Lewis Berger & Sons Ltd., B.P. 611,109
[43] Sherwin-Williams Co., U.S.P. 2,457,769; *Chem. Abs.*, 1949, **43**, 2448e
[44] Nagy, D. A. and British Industrial Plastics, Ltd., B.P. 632,335
[45] Sherwin-Williams Co., U.S.P. 2,457,768; *Paint Oil Chem. Rev.*, No. 131, 436
[46] Resinous Products and Chemical Co., B.P. 614,532
[47] I.C.I. Ltd., B.P. 616,453; *Paint Oil Chem. Rev.*, No. 131, 469
[48] Shawinigan Chemicals Ltd., B.P. 615,723
[49] Scheifel, B. F. H., *Farbe u. Lack*, 1948, **54**, 200
[50] Oakley, J. E., Reichard H. and Vinyl Products Ltd., B.P. 611,904
[51] Du Pont de Nemours & Co., U.S.P. 2,397,724
[52] Moses, S., *Ind. Eng. Chem.*, 1949, **41**, 2338
[53] McLaren, A. D. and Seiler, C. J., *J. Polymer Sci.*, 1949, **4**, No. 1, 63
[54] B.T.H. Co. Ltd., B.P. 626,515
[55] Hurd, D. T. and Roedel, G. F., *Ind. Eng. Chem.*, 1948, **40**, 2078
[56] Pittsburgh Plate Glass Co., U.S.P. 2,394,642
[57] B.T.H. Co., Ltd., B.P. 629,138
[58] Kline, G. M., *Ind. Eng. Chem.*, 1949, **41**, 2133
[59] Phillips, L. N., B.P. 625,847
[60] *Chem. Industr.*, 1946, **60**, 814; *Paint. Varn. Prod. Mgr.*, 1949, **29**, 58; *Paint Oil Chem. Rev.*, No. 129, 227
[61] Jones, J. Idris, *J. Soc. chem. Ind.*, 1949, **68**, 225
[62] *Chem. Industr.*, 1949, **63**, 181
[63] Pittsburgh Plate Glass Co., U.S.P. 2,397,600
[64] Chatfield, H. W., *Paint Manuf.*, 1950, **20**, 6

DRYING OILS, DRIERS AND VARNISHES (J. H. Greaves, B.Sc., A.R.I.C.)

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METHODS for modifying properties of unsaturated oils with a view to improvement, e.g. to obtain increased drying power, or sometimes for a specific purpose, such as the requirement of non-yellowing, continue to be investigated and described. A problem of theoretical importance—whether linseed oil polymerizes through an intermediate conjugated stage or by some other mechanism—still gives rise to informatory discussion.

Drying oils

The supply of drying oils is a problem which has continuously to be studied from several aspects. For this country in 1949 linseed, tung and dehydrated castor oils have continued to be the most important drying oils ; stillingia, tobaccoseed, oiticica and tall oils are the only alternatives. There is little change to report on indigenous linseed oil. Some tung oil,[1] from *Aleurites fordii*, has been imported from Brazil[2] and Argentina[3] and some, chiefly from *A. montana*, from Nyasaland. The new fatty acid in stillingia oil has been identified by T. P. Hilditch[4] as the conjugated 2 : 4-decadienoic acid. Tobaccoseed oil, a semi-drying oil used mostly in admixture with tung oil to improve the drying properties, has been analysed by S. D. Mahant and P. N. Pandit,[5] and examined for industrial utilization by M. Narasimha Rao and S. M. Ramanayya.[6] Oils from several oilseeds grown in Australia have been described, notably tung oil (by A. R. Penfold)[7] and linseed oil and others (by L. S. Cash[8] and G. Winter and W. Nunn).[9] Among many miscellaneous oils which have been reported upon there are some which may in due course become of economic and technical importance, such as those from the seeds of *Euphorbia marginata* (described by N. A. Albertsma)[10] or from the Brazilian cotia nut (described by M. da C. P. B. Cavalcanti).[11]

The separation from an oil of a portion with improved drying properties, necessitating a second portion with decreased or non-drying properties, has been performed in many ways. Solvent extraction processes have now been described in more detail. On a manufacturing scale solvent segregation (or fractionation) is carried out in vertical towers filled with packing material, the oil and solvent passing in opposite directions. The use of propane (under sufficient pressure to liquefy it) as the solvent has been described by H. J. Passino.[12] The more unsaturated glycerides are less soluble in the propane so that separation of an improved drying fraction of higher iodine value is readily obtained. Although this is the converse of the furfuraldehyde process,[13] where the solvent preferentially dissolves the glycerides of greater unsaturation, there appears to be no fundamental difference between the two processes. The differences, other than those connected with economics, may be those related to the removal of non-glyceride constituents, such as colouring matter and free acids. S. W. Gloyer[14] and S. E. Freeman[15] describe how refined and fractionated soya-bean oil can be obtained in substantially one process

from crude oil by extraction with furfuraldehyde and then in another column with (American) naphtha. Chromatography has been widely used in analytical techniques for separation of triglycerides, and H. Weil[16] has described the application of this technique to separations on the commercial scale.

Another method of obtaining an improvement in drying is the actual removal of non-drying glycerides by the use of steam (Öl- u. Chemie Werk[17]). As regards production of conjugated double-bond systems in fatty acid chains by heating with excess alkali, there is no fresh progress to report. H. M. Teeter, R. C. Bachmann, E. W. Bell and J. C. Cowan[18] describe how soya-bean oil can be chlorinated with *tert.*-butyl hypochlorite to furnish chlorinated oils containing about 10% chlorine and up to 20% conjugation. The mechanism is probably

$$\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot \rightarrow \cdot CHCl\cdot CH{:}CH\cdot CH{:}CH\cdot .$$

Reduction of the unsaturation of linseed oil has been described by F. G. Smith[19] as bringing about an improvement in a novel direction. When this oil is partially hydrogenated so as to reduce the linolenic acid content to a comparatively small figure the product is an oil still having good drying properties and distinct non-yellowing characteristics.

The fatty acid chains in the molecules of triglyceride oils can be made to undergo chemical reaction with many substances with production of a desirable product. Two substances used are maleic anhydride and styrene ($C_6H_5\cdot CH{:}CH_2$) to produce maleinized and styrenated oils respectively. H. Plimmer[20] has described the reaction of maleic anhydride at 200° C. with linoleic chains in the form of the free acid or as the methyl ester. There is condensation with the saturation of one double bond. After reaction with methyl oleate, however, the unsaturation remains unchanged. In these reactions there is loss of acidity not fully accounted for by decarboxylation as measured by carbon dioxide evolved. It is suggested that carboxyl groups are also destroyed by condensation reactions.

Information concerning the preparation of styrenated oils is now being presented in steadily increasing quantity. The various procedures described for reacting styrene with drying oils have been classified[21] into three methods: (i) emulsion methods, (ii) solvent methods and (iii) mass methods. Reaction in an emulsion form receives little mention in recent literature.[22] The effect of different solvents when the styrenation is carried out in solution has been described by F. Armitage, D. H. Hewitt and J. J. Sleightholme.[23] Relative patents have been taken out by L. Berger and Sons Ltd., using such oils as linseed stand oil, dehydrated castor oil, blown linseed oil, oiticica oil[24] and also unsaturated fatty acids.[25] In the so-called mass-methods the use of inert solvents in order to obtain homogeneous clear products is avoided by the Dow Chemical Co.,[21,26] by the addition of α-methylstyrene, a compound somewhat less reactive than styrene itself. The properties of styrenated oils vary, of course, with the starting materials, and the method used, but the results of some experiments of the Detroit Paint and Varnish Production Club[27] are of interest. Using soya-bean, dehydrated castor, blown linseed and blown soya-bean oils good pigment-wetting properties are obtained, and films

show good flexibility, poor mar resistance, excellent colour and colour retention, and superior water-vapour resistance but poor solvent resistance. N. R. Peterson[28] has stated that some styrenated oils (prepared by the methylstyrene method) give films which are petroleum-soluble and thermoplastic. By starting with oxidized oils, cross-linked molecules are formed which confer petroleum resistance and thermal stability.

Oxidation

Reviews in the field of oxidation include those by D. Swern, J. T. Scanlan, and H. B. Knight,[29] who cover the period from 1941, and by P. O. Powers.[30] In line with most currently accepted views Powers gives the successive stages of oxidation of drying oils as (i) peroxide formation, (ii) peroxide decomposition, (iii) polymerization, and (iv) degradative oxidation. It is probable that both cyclic peroxides and hydroperoxides are formed, decomposition being by dehydration and reduction. Subsequent polymerization appears to be more likely to take place by carbon to carbon linkages than by a process involving carbon to oxygen links. Formation of conjugated dienes during oxidation of methyl esters of linoleic and linolenic acids continues to be observed; absorption spectra measurements are employed. J. R. Chipault and W. O. Lundberg[31] deduce from a direct relationship between peroxide values and extinction coefficients at 232·5 mμ. for methyl linoleate oxidized at 40° C. that some stable peroxides formed are conjugated dienes. More than one type of diene ketone is probably formed. W. R. Lewis and F. W. Quackenbush,[32] using the polarograph, have found different peroxide structures which could not be separated by chromatography. After methyl linoleate has absorbed two molecules of oxygen, W. Treibs[33] finds that two atoms are present as peroxide and that the other two behave on analysis as an ester group. Infra-red spectra have been used by F. J. Horn, I. I. Bexman and B. F. Daubert[34] to examine linseed oil before and after oxidation, with the result that formation of geometrical isomers of the original constituent fatty acids is shown. Oxidation of linseed oil at different temperatures has been examined by N. W. Gillam,[35] who describes several different mechanisms favoured by different reaction temperatures. At room temperatures olefinic linkages are not readily attacked and hydroperoxide groups are first formed. At 100° to 120° C. peroxides are formed by attack at a double bond and decompose to acids. There is also some esterification. At 150° to 200° C. unstable peroxide intermediates are formed without an induction period. At 200° C. these intermediates produce polymers similar to those obtained by heat. There is no doubt that ideas concerning complicated reactions such as those which occur during oxidation of linseed oil are clarified by study of the simpler oxidation processes undergone by, say, methyl linoleate. Nevertheless, how closely the fatty acid chains in triglyceride oils coincide with the single chain in methyl esters as regards the course of oxidation, and also of polymerization is a matter of conjecture.

Polymerization

Polymerization, in a wide sense, with some manufacturing processes, has been reviewed by C. C. Winding.[36] It may be noted that continuous

methods of processing oils are described more and more frequently, for polymerizing oils (by R. A. Carleton[37] and H. L. Barnebey[38]) and the dehydration of castor oil (E. Sutherland and C. W. Andrews[39]). In the allied field of fatty acid manufacture, continuous methods of hydrolysis and distillation are well known (e.g. Proctor and Gamble Co.[40]).

E. H. Farmer[41] has presented some views on a mechanism for polymerization of drying oils, including discussion of such matters as electron movements in the molecules and their influence of these on this course of reaction. Referring to this paper, I. M. Bernstein[42] states that Farmer does not attach sufficient importance to steric factors such as steric hindrance and *cis–trans* isomerism. In a reply Farmer[43] emphasizes that the mechanism of polymerization presented does not entail the formation of conjugated molecules. On the other hand, J. S. Long,[44] in a discussion of the mechanism of film formation, draws attention to the work of R. F. Pashke and D. H. Wheeler[45] on the thermal polymerization of methyl linoleate. An apparent first order reaction is found for disappearance of linoleate, and it appears that dimers are formed by an addition reaction between normal (original) linoleate and conjugated linoleate. L. V. Anderson and J. V. Porter[46] have attempted to correlate polymerization rates with the fatty acid composition of non-conjugated naturally occurring oils. The function 2·0 (% linolenic acid) + 1·6 (% linoleic acid) + 0·6 (% oleic acid) gives a figure which predicts the polymerization rate up to 100 poises better than the iodine value. The contribution of oleic acid is unexpectedly high; it apparently plays an important part in the stage when three dimensional polymers are being formed.

Driers

Driers prepared from various organic acids continue to be examined in some detail with really little difference in behaviour between most radicals. J. T. Horta[47] discusses the part played by the acid radical in assisting solution of drier metal soaps in oils and finds that driers prepared from olive oil and copra oil are as good as those from linseed oil. Particularly good results are given by cobalt stearate, oleate, and caprylate. Driers from 2-ethylhexoic acid have been compared with naphthenates by C. A. Klebsattel,[48] and R. Dooper and F. J. Hermann,[49] who find great similarity between both types, sometimes one radical showing to advantage, and sometimes the other, according to the factor being investigated.

Varnishes

Variations in cooking times with temperature of a phenolic resin–tung oil varnish has led F. J. Hermann[50] to a method for testing the degree of cook. After a certain period the string test is no longer of use as an indication of real differences in progress of the cook. The per cent acetone-insoluble fraction increases steadily during heating, and an acetone dilution test is of greater value. The relation between viscosity and acetone insolubility is independent of the temperature.

Analysis

Microanalytical techniques in oil and fat chemistry (reviewed by N. Kretchmer[51]) are proving of continuously greater value in analysis, even though many of the methods are still largely experimental. C. Whalley[52] has described determination of oxygen in oils and of water. Another micro-determination is of peroxides by colorimetry (P. Dubouloz, M. F. Monge-Hedde and J. Fondarai[53]); oleic and linoleic acids can be micro-detected by oxidation to dihydroxystearic acid and sativic acid respectively (G. Gorbach and H. Malissa[54]). Estimation of hydroxyl values on 0·1g. samples have been described by H. Nobori and T. Yamada.[55]

Although J. Baltes[56] claims that thiocyanogen values of pure linoleic and linolenic acids are reproducible constants, J. D. von Mikusch[57] maintains that use of empirical figures are necessary, since the results obtained vary with experimental conditions.

References

1 B.S. 391 : 1949
2 Neto, A. S., *An. Assoc. quim. Brazil*, 1948, **7**, 89
3 Provisional Official IRAM Standard 1027-NP
4 *J. Oil Col. Chem. Ass.*, 1949, **32**, 5
5 *J. sci. Industr. Res. India*, 1948, **7 A**, 229
6 Ibid., 1948, **7 B**, 87
7 *J. Oil Col. Chem. Ass.*, 1948, **31**, 299
8 *Paint Notes, Aust.*, 1948, **3**, 12
9 Ibid., 1948, **3**, 43
10 *Paint Manuf.*, 1949, **19**, 135
11 Inst. Nac. de Tech., 1947, Special Rept.
12 *Ind. Eng. Chem.*, 1949, **41**, 280
13 Annual Reports, 1948, 378
14 *J. Amer. Oil Chem. Soc.*, 1949, **26**, 162
15 Assr. to Pittsburgh Plate Glass Co., U.S.P. 2,390,528
16 *Paint Technol.*, 1949, **14**, 391, 439
17 B.P. 593,569
18 *Ind. Eng. Chem.*, 1949, **41**, 849
19 *J. Amer. Oil Chem. Soc.*, 1948, **25**, 328
20 *J. Oil Col. Chem. Ass.*, 1948, **31**, 431 ; 1949, **32**, 99
21 The Dow Chemical Co., 'Styrenated Drying Oils'
22 Cf. L. Berger & Sons Ltd., Wakeford, L. E., Hewitt, D. H. and Armitage, F., B.P. 609,750
23 *J. Oil Col. Chem. Ass.*, 1948, **31**, 437
24 B.P. 605,929
25 B.P. 611,109
26 U.S.P. 2,468,798 ; *Chem. Abs.*, 1949, **43**, No. 14, 5639b
27 *Amer. Paint J. Conv. Daily*, 1948, **33**, No. 6B, 33
28 *Amer. Paint J.*, 1948, **32**, 32
29 *J. Amer. Oil Chem. Soc.*, 1948, **25**, 193
30 *Ind. Eng. Chem.*, 1949, **41**, 304
31 Hormel Inst. Univ. Minnesota Ann. Rep., 1946–47, 9
32 *J. Amer. Oil Chem. Soc.*, 1949, **26**, 53
33 *Chem. Ber.*, 1948, **81**, 472
34 *J. Amer. chem. Soc.*, 1949, **71**, 812
35 *J. Aust. chem. Inst.*, 1949, **16**, 19
36 *Ind. Eng. Chem.*, 1948, **40**, 1643
37 B.P. 617,151
38 *J. Amer. Oil Chem. Soc.*, 1949, **26**, 493
39 *J. Oil Col. Chem. Ass.*, 1949, **32**, 511
40 B.P. 617,929

[41] *J. Oil Col. Chem. Ass.*, 1948, **31**, 393
[42] Ibid., 1949, **32**, 84
[43] Ibid., 86
[44] Ibid., 377
[45] *J. Amer. Oil Chem. Soc.*, 1949, **26**, 278
[46] *Ind. Eng. Chem.*, 1949, **41**, 741
[47] *Acero y Energia, Barcelona*, 1947, **4**, 24; *Chim. et Industr.*, 1949, **61**, 55
[48] Off. Dig. Fec. Paint Var. Prod. Cl., 1948, No. 284, 686
[49] *Verfkroniek*, 1949, **22**, 25
[50] C.I.M.O., 1949, Circ. 55; P.R.S. Abs., 1949, 317
[51] *J. Amer. Oil Chem. Soc.*, 1948, **25**, 404
[52] *Paint Technol.*, 1949, **14**, 59
[53] *Bull. Soc. chim. Fr.*, 1947, Fos. 9–10, M. 900–1; P.R.S. Abs., 1948, 357
[54] *Mikrochem. mikrochim. Acta*, 1947, **33**, 145; *Chem. Abs.*, 1948, **42**, 1748 f.
[55] *J. Soc. chem. Ind., Japan*, 1944, **47**, 15; *Chem. Abs.*, 1948, **42**, 6554c
[56] *Farbe u. Lack*, 1948, **54**, 268
[57] Ibid., 238

PAINTS AND PIGMENTS (L. J. Brooks, A.R.I.C.)

Henry Clark and Sons Ltd.

Anti-corrosion paints and pigments

DURING the period under review the many aspects of corrosion and paint continue to be widely studied. The general electrochemical theory of corrosion is increasingly applied in the development of pigments which may be considered to exercise an inhibitive influence on the progress of the electrolytic reaction, e.g. either by cathodic protection, or anodic passivation by soluble or basic pigments.[1] In the same manner considerations are given to the extent to which the organic binder of the paint may contribute a desirable degree of ohmic resistance between anodic and cathodic parts which might otherwise constitute the elements of an active galvanic couple. An experimental polystyrene film is shown, for example,[2] to exert initial protection in this manner, but its protective properties deteriorate with the progressive sorption of water; this is followed by inward migration of ions stimulated by a process of osmosis and possible electro-endosmosis. Similar physico-chemical considerations are advanced[3] which emphasize the importance of the capillary properties of the coatings in determining the influence of electro-osmotic forces on corrosion under paint films. It is suggested, for example, that a negative wall-charge is necessary for electro-osmotic dehydration, a process which may be effected by lead or zinc pigments dispersed in oil media the particles of which acquire a negative charge owing to the surrounding film of metal soap.

A related study[4] of blistering of paint films on metal immersed in sea-water also lends support to this physico-chemical mechanism, where it is considered that films act first as swelling gels and then as imperfect semi-permeable membranes. The experimental evidence indicates that the blister-water possesses a lower chloride concentration and a higher p_H than the sea-water environment of the film. It is considered that local electrolytic cells are responsible for this accumulation of hydroxyl ions

which eventually destroy adhesion between the metal and the film; the blister is then formed by osmotic expansion.

Although the electrical concept of corrosion is of course no longer new, it is nevertheless interesting to note the growing confidence with which it is applied. This is reflected, for example, in the increasing use of electrical methods of predicting the performance of metal protective paints. One investigator, for example,[5] describes a method for determining polarization, time/potential curves and film resistance, and it is claimed that these values may be observed as functions of the corrosion process.

A similar electrical technique[6] describes the particular case of untreated and phosphated metal surfaces. That some caution however, is desirable in interpreting these electrical methods is implied by recent electrode-potential measurements[7] on painted steel immersed in saline solution. It is considered necessary to continue the experimental observations for some considerable time before attaching any significance to the potential/time relation.

Although the electrochemical role of individual anti-corrosion pigments is generally accepted, their influence in protecting iron from corrosion is considered by one investigator[8] to be over-estimated and only becomes operative when the film is deteriorating. However this may be, the interest in such pigments is very great and continues to be expressed in numerous papers describing their preparation, properties, mechanism and application.

Of these anti-corrosion pigments zinc chromates, red lead and aluminium continue to be the most actively investigated components of protective primers for metals; metallic zinc pigmented paints have also received attention, and a recent review[9] advances the opinion that these are most suitable for ships.

The value of the zinc chromes in primers for light alloys is generally confirmed[10,11] but this unanimity of opinion is not extended to the protection of steel, which appears to invite a much wider range of suitable systems of sharply competitive interest. Zinc chromes and red lead are still the most favourably reported materials, as indicated, for example,[12] in recent marine exposure-tests on steel panels using vehicles based on various combinations of linseed, oiticica and tung oil with black East India and Congo copals. These conclusions appear to be confirmed by an incomplete progress report of atmospheric exposure tests conducted by the New England Paint and Varnish Production Club[13] using linseed oil and alkyd vehicles; so far the zinc chrome and red lead primers are said to be superior to white lead, iron oxide and aluminium primers.

It is difficult to assess the numerous and sometimes conflicting claims made for protective systems on steel, as the conditions of test and composition of vehicle are seldom strictly comparable; but in one comprehensive Swedish report[14] covering a nine years' corrosion investigation of 21 primers and 50 finishing coats, favourable mention is made of micaceous iron oxide/aluminium intermediate and finishing coats over red lead primers. In addition white lead and white lead/aluminium finishing coats in a polymerized-oil medium are said to have given very good results.

The notable interest in zinc chromate primers is further displayed in contributions by H. Rabaté[15] and H. B. Kirkpatrick[16] who share similar views regarding the basic/oxidizing mechanism of the pigment in preventing corrosion, and the importance of a limited and strictly controlled solubility; the commonly held view that this is best achieved by ensuring the complete absence of 'soluble salts' is confirmed by Kirkpatrick[16] who claims that such measure will eliminate the defect of blistering commonly attributed to such primers, and that a high-phthalic linseed oil alkyd is the best medium to maintain an optimum concentration of soluble chromate ions in the vicinity of the metal. Rabaté[15] also provides comparative analytical figures for the composition of the three main types of basic zinc chromate (*a*) the English or French type represented by the empirical formula $K_2O,4ZnO,4CrO_4$; (*b*) the American developed zinc tetrahydroxychromate: $ZnCrO_4,4Zn(OH)_2$, and a third type (*c*) the trihydroxychromate $ZnCrO_4,3\ Zn(OH)_2$, which is claimed to be of interest as it has a low water solubility and is easily prepared.

The conflicting claims made for red lead and zinc chromate for use in marine primers find expression in an investigation of primers for marine atmospheric environment[17] where it is claimed that combinations of red lead and zinc chrome in fast-drying synthetic resin media are superior to either conventional red lead or zinc chromate primers alone. The investigation has been conducted over a period of 41 months in the Marine Basin at Sayville, Long Island on plates exposed just above the water.

Finally, the general case of zinc chromate *versus* red lead is reviewed by T. P. Brown,[18] who summarizes the economic and practical reasons for its adoption by the U.S. Navy in place of red lead.

Although authors generally have been concerned with the more practical aspects of chromate primers, attempts have also been made to study the fundamental mechanism of chromate passivation of which the current theories assume either the formation of a thin layer of insoluble chromate or an adsorbed layer of chromate ions. J. E. O. Mayne and M. J. Pryor[19] have, however, studied the inhibition of corrosion of steel immersed in aerated solutions of chromic oxide and potassium chromate and suggest the formation of a thin impervious film of γ-Fe_2O_3 by oxidation of the iron ions while still in the solid lattice.

Certain criticisms previously mentioned of both zinc chromate and red lead appear to have prompted the development of barium potassium chromate and chromated red lead. Both of these are included as effective anti-corrosion pigments in a study of various commercial red leads.[20] Barium potassium chromate is a relatively new addition to the chromate series and its production on a pilot scale by the dissociation of potassium dichromate at 500–650° c. in the presence of barium carbonate is described.[21] It is claimed to possess the familiar anti-corrosion characteristics of zinc chromate, with the advantages of a purer molecular entity and superior pigmentary properties; the latter are said to include: light weight, low oil absorption, freedom from 'soluble salts,' softness of texture, and compatibility with a wide range of media. It is also claimed to toughen rather than embrittle the film, and these distinctive properties are said to have been confirmed by the results of six years' exposure tests.

Finally one may conclude this review of anti-corrosion paints and pigments by noting the further claims[22] made for the anti-corrosive and general paint properties of the German pigment lead cyanamide.

Anti-fouling compositions

There is little to report on the subject of anti-fouling compositions but the familiar conception of 'leaching rate' in determining the behaviour of anti-fouling paints is the subject of a further interesting contribution by H. Barnes.[23] This author has examined the influence of pigment concentration at the surface of the film on the initial leaching-rate curve, and has considered the practical consequences of a surface deficiency of Cu_2O. The effect of an overlying layer of varnish film may well delay the initial development of a suitable leaching rate at a critical stage in the life of the film. That this may occur with anti-fouling paints of apparently identical and otherwise standard composition adds a further complication to an already complex subject.

From time to time attempts are made to replace conventional copper and mercury compounds in anti-fouling paints by even more toxic ingredients; these attempts have generally proved of transient interest. Considerable claims are made,[24] however, for the use of a complex condensation product formed by the reaction of certain simple aliphatic or aromatic aldehydes with complex tri-substituted phenols of the general formula 1 : 4 : 3 : 5- or 1 : 2 : 3 : 5-$OH{\cdot}C_6H_2RR'_2$, in which R may be phenyl or (*cyclo*)-alkyl, and R' may be H or R. The product may be used in a short-oil varnish medium and is said to be particularly effective against barnacles.

Manufacture of paints and pigments

Of other pigments in normal use in paints there appear to be few outstanding developments to report, although many claims still continue to be made for various improvements in detail.

There is an increasing emphasis on methods for promoting continuous production of pigments and/or paints, and this trend appears, for example, in the description of a new process for manufacturing lead chromes.[25] The feature of this method is the complete or partial elimination of the usual vat-batch process, with considerable saving in production time. It is claimed to be applicable to the manufacture of lead chromes, zinc chromes and molybdate-orange colours. The process consists in the use of a series of small reaction chambers into which the reactants (e.g. lead nitrate, sodium chromate, and sodium sulphate) are introduced, and in which the precipitated slurry from the first reactor is treated with other additives, and the particle size adjusted by controlling the temperature and p_H. The final wet filter-cake is rolled into rods, dried, and pulverized.

One notes the appearance on the market of very finely ground natural iron oxides, barytes and other pigments in which reduction of particle size to micron dimensions is effected by treatment of the coarsely ground material with a stream of superheated steam or compressed air at very high pressure and velocity. A detailed description is given[26] of certain mills of this type, termed 'fluid energy mills' in which claims are made for

the greatly improved pigmentary properties of these micron-ground materials; lower oil absorption and resistance to agglomeration are, for example, attributed to the smooth rounded character of the discrete particles. Another feature of this type of mill, which incidentally includes no moving mechanical parts, is said to be the ready dehydration of pigment filter-cakes without overheating. This leads to the suggestion that at a certain point a paint vehicle could be introduced and a finished paint prepared direct from the dry or wet filter cake; this obviates many of the normal operations of paint manufacture, and affords yet another instance of a movement towards 'continuous production.' This tendency to reduce or eliminate mechanical 'grinding' aids receives further expression in a short description[27] of pigment dispersion by 'flushing.' The familiar application of this principle of preferential wetting to, for example, the preparation of ground white lead is of course well-known, but it is interesting to note its extension to pigments generally, and again to note its suggested application as an immediate preliminary to the preparation of a finished paint. The practicability of these developments is said to be due to the wide range of modern wetting agents available, and to the special construction of the flushing machine which includes provision for steam-jacket heating and operation under reduced pressure. Similar applications of the flushing technique are described by A. F. Schmutzler and D. F. Othmer.[28]

Oil absorption and film formation

The determination of the 'simple' property of oil absorption of pigments is known to every student of paints and pigments but the scientific validity of the standard methods of determining this property has been in doubt in recent years. A cooperative investigation conducted by the Bristol Section of the Oil and Colour Chemists' Association in 1945 had revealed wide discrepancies between the results of different operators using a standard method. The variations were considered inadmissible in a scientific test, and the results obtained were therefore made the subject of critical analysis by E. Marsden.[29] From this it appears that the lack of reproducibility between different operators is due to the fact that the apparently simple operation of determining 'oil absorption' really involves the simultaneous determination of two distinct properties of the pigment, i.e. an 'oil-coating term' largely conditioned by the personal factor of the operator, and an 'oil-adsorption term' representing a truer constant characteristic of the pigment and oil and independent of the technique. These views are considered to be supported by a detailed mathematical analysis of the results and by practical oil-absorption determinations on a series of experimental ferric oxides of increasing particle size.

The mechanism of film formation and deterioration has long been a matter of investigation and the period under review includes further contributions to this complex subject. The important Oil and Colour Chemists' Association Conference at Rothesay,[30] for example, was devoted to discussion of the many aspects of 'Films and Film Formation.' In particular J. S. Long[31] presented a comprehensive review of recent information relating to fims formed by oxidation, as studied by the

American Federation of Production Clubs. The review includes electron-micrograph studies of simple linseed-oil films during the process of drying, which are considered to support a mechanism based on the progressive development of micelles. Some interesting new data are also given on the exceptional film properties of the epichlorohydrin bisphenol esters of drying, semi-drying and even non-drying oil fatty acids. The advantages conferred by these polymeric polyhydric alcohols on combinations with ordinary fatty acids are said to be due to their high molecular weight, and to the large number of reactive hydroxyl groups available (5–15 as compared with 3 and 4 for glycerol and pentaerythritol respectively). In the same review J. S. Long also discusses film properties in terms of the mechanical requirements of civil engineering, i.e. tensile strength, percentage of elongation, modulus of elasticity, etc. and shows how these features become operative in the strains and stresses communicated by engineering and railway structures. It was therefore considered that the wide range of modern high-polymer resin and oil combinations should permit the formation of functional coatings possessing the desired mechanical properties. The influence of water, ultra-violet light, and temperature changes in promoting film deterioration was also discussed by J. S. Long.

Titanium dioxide pigments

The special case of photochemical reactivity and the familiar chalking of titanium dioxide pigments has been examined by A. E. Jacobsen[32] who claims to have established a complete analogy between the Renz test (in which TiO_2 is photochemically reduced in the presence of mandelic acid to a lower oxide identified as Ti_2O_3), and the atmospheric chalking of TiO_2 dispersed in oxidizable organic media. It is considered from the evidence of light-reflectance studies that the reaction in both cases is reversible on the removal of the actinic rays; and that both anatase and rutile types are photochemically reactive. It is considered highly probable that the life of a titanium pigmented paint under ordinary weathering is influenced by a cycle of such redox phenomena.

The general character of modern rutile-type titanium pigments is the subject of a contribution by S. G. Tinsley and A. Bowman,[33] which includes a discussion of the crystalline modifications of titanium dioxide as identified by X-ray methods and the correlation of their physical properties with pigmentary properties and paint performance. The results of exposure and field tests using the new rutile type are considered to confirm its superiority, in durability and tint retention, to other conventional white pigments, such as zinc oxide, white lead, or antimony oxide.

Other titanium dioxide investigations include the use of the electron microscope as an instrument for the study of its dispersibility in various solvents and paint vehicles[34] on the presumption that the gloss of an enamel finish is related to the completeness of dispersion. Heptane was chosen as an example of a poor dispersing solvent for titanium dioxide and the effect of adding small quantities of 35 surface-active agents was examined. These consisted of alcohols, esters, cyclic compounds and organo-metallic compounds, and of these only the metallic compounds are

said to have had any significant effect in improving the dispersion of titanium dioxide in heptane. The metal-containing additives included the naphthenates of lead, calcium and zinc, and calcium petrosulphonate and lead 2-ethyl hexoate. Similar studies are proceeding with actual enamel media utilizing a gold-shadowing technique in which the sample is studied *in vacuo* in the vicinity of a heated gold filament; surface irregularities are silhouetted on being struck by the particles of vaporized gold.

The interest in good dispersion is shown by even more practical studies of the milling of titanium dioxide in alkyd/white spirit media in pebble mills.[35] The classical principles of ball-milling are critically examined and it is claimed that improved dispersion of grinding pastes containing only 50% pigment and 50% resin solution may be effected by operating above room temperature. At the same time it is considered that better dispersion in a shorter time and at lower temperature is promoted by increasing the white spirit content, and in fact it is considered that the wetting action of the mineral spirits is a greater controlling factor than the size of grinding media employed.

The possibilities of ultrasonic wave dispersion of pigments is under investigation by the Pittsburgh Club and the results of a preliminary study are reported.[36] The pigments examined included chrome yellow, carbon black, titanium dioxide and toluidine toner. The conditions are exacting and require careful attention to mass, pigment concentration, viscosity, amplitude of vibration and time, but nevertheless, satisfactory dispersions are claimed and the results appear to be promising.

References

1 Mayne, J. E. O., 1er Congrès Tech. Internat. Ind. Peint. Paris, 1947, 261

2 Idem, Oil Col. Chem. Assoc. Conf. Rothesay, 1949; *J. Oil Col. Chem. Ass.*, 1949, **32**, 481

3 Wirth, J. K., *Arch. Metallk.*, 1947, **1**, 445, 452; *Chem. Abs.*, 1948, **42**, 7224b, 7695d

4 Gay, P. J., Oil Col. Chem. Assoc. Conf., Rothesay 1949; *J. Oil Col. Chem. Ass.*, 1949, **32**, 488

5 Shaw, W. E. and Hawke, D. L., *Can. Paint Varn. Mag.*, 1949, **23**, 18, 40, 42

6 Jaudon, E., *Metaux, Corrosion, Usure*, 1944, **19**, 12; *J. Iron Steel Inst.*, 1948, **159**, 346

7 Wormell, F. and Brasher, D. M., *J. Iron Steel Inst.*, 1949, **162**, Pt. 2, 129; *J. Brit. Shipbuild. Res. Ass.*, 1949, **4**, 337

8 Wagner, H., *Arch. Metallk.*, 1947, **1**, 448

9 Hoskings, A. W., *Ship & Boat Builder*, 1949, **3**, 17; *J. Brit. Shipbuild. Res. Ass.* 1949, **4**, 384

10 Rigg, J. G. and Skerry, E. W., *J. Inst. Metals*, 1948, **75**, 69; *Bull. Brit. non-ferr. Met.*, 1948, **28**, 398

11 Kirkpatrick, H. B., *J. Oil Col. Chem. Ass.*, 1949, **32**, 223

12 American Gum Importers Labs., *Can. Paint. Varn. Mag.*, 1948, **22**, 16, 48

13 New England Paint & Varn. Prodn. Club, Progress Report IV, *Amer. Paint J. Conv. Daily*, 1948, **33**, 8, 10, 26, 28, 30; 28, 30, 32; *Off. Dig. Fed. Paint Varn. Prod. Cl.*, 1949, **298**, 792

14 Tengstrand, G., *Farg och Fernissa*, 1948, **12**, 81, 103, 136, 155, 171, 177

15 Rabaté, H., *Chim. peint.*, 1949, **12**, 164, 286

16 Kirkpatrick, H. B., *J. Oil Col. Chem. Ass.*, 1949, **32**, 223

17 Vander Valk, C. J., *Off. Dig. Fed. Paint Varn. Prod. Cl.*, 1949, **292**, 260

18 Brown, T. P., '*By Gum*,' 1949, **20**, No. 5, 10

19 Mayne, J. E. O. and Pryor, M. J., *J. chem. Soc.*, **1949**, 1831

20 Frydlender, J. H., *Nev. Prod. Chim.*, 1947, **50**, 40

21 Eickhoff, A. J. and Kebrich, L. M., *Paint Oil Chem. Rev.*, 1949, **112**, 18, 39; *Off. Dig. Paint Varn. Prod. Cl.*, 1949, **291**, 188

[22] I.G. Farbenindustrie, Consultants Bureau, Metal Abs. List No. 1. PVL.–1
[23] Barnes, *J. Iron Steel Inst.*, 1949, **162**, 179
[24] Stoner Mudge Inc., U.S.P. 2,398,069
[25] Williams, R. junr., *Chem. Engng.*, 1949, **56**, 121
[26] Stephanoff, N. N., *Off. Dig. Paint Varn. Prod. Cl.*, 1949, **296**, 590
[27] Parle, W. C., ibid., 1949, **296**, 606
[28] Schmutzler, A. F. and Othmer, D. F., *Brit. Abs.*, 1949, B II, 1041
[29] Marsden, E., *J. Oil Col. Chem. Ass.*, 1949, **32**, 183
[30] O.C.C.A. Conference, Rothesay, 1949, ibid., 377, 481, 511
[31] Long, J. S., ibid., 377
[32] Jacobsen, A. E., *Ind. Eng. Chem.*, 1949, **41**, 523
[33] Tinsley, S. G. and Bowman, A., *J. Oil Col. Chem. Ass.*, 1949, **32**, 233
[34] Von Fischer, W., Trantman, W. D. and Friedman, J., *Off. Dig. Paint Varn. Prod. Cl.*, 1949, **298**, 843
[35] Baker, C. P. and Vozella, J. F., ibid., **294**, 433
[36] Pittsburgh Club, ibid., **298**, 781

CELLULOSE ESTER AND ETHER LACQUERS (H. L. Howard, B.Sc., A.R.C.S., D.I.C., M.I.Chem.E., F.R.I.C.)

DEVELOPMENTS over the last few years have resulted in the modification of cellulose acetate by the introduction of mixed fatty acid esters and the establishment of the 'melt-coating' technique. The optimum properties are developed in the cellulose acetate–butyrate esters and the comprehensive range of low viscosity types now available commercially have been the subject of a communication by C. J. Malm and H. L. Smith.[1] Compared with cellulose acetate, the lower moisture regain indicates improved dimensional stability; in compatibility with plasticizers and improved solubility characteristics they approximate more closely than before to the range of low-viscosity cellulose nitrates. Their stability to ultra-violet light is further improved by the addition of 1 to 2% *m*-benzyl phenyl ether[2] or, still better, methyl resorcinol ether.[3] Under the influence of heat, ethyl cellulose suffers oxidation with loss of ethoxyl content and a lowering of viscosity. McBurney[4] attributes this to hydroperoxide formation followed by chain scission; oxidation can be considerably reduced by the addition of 1% diphenylamine. Under the influence of ultra-violet light oxidation is greatly accelerated, but the mechanism is identical[5]; menthylphenol and hydroquinone monobenzyl ether were found to be effective antioxidants.[5] Under comparable conditions of heat (90° c.) cellulose acetate could not be oxidized[6] but at higher temperatures (160° c.) degradation occurs; it is preceded, however, by an induction period which may vary considerably with different samples and under varying conditions. Evidence is adduced that carbon monoxide is evolved, but definite identification is lacking. For these reasons, the authors consider that the usual heat-test for the stability of cellulose acetate can be very misleading, and suggest that the induction period or the length of time to produce a given degree of discoloration would be more reliable. Attempts to phosphorylate cellulose by means of phosphorus oxychloride and pyridine[7] rendered the material flame-proof but the fibre structure was largely destroyed. In the presence of urea the destruction is considerably reduced. Ethyl cellulose and cellulose acetate are however

readily phosphorylated under these conditions. In the presence of urea the phosphate group is shown to be present largely in the form of the mono-ester,[8] but in its absence amounts of di-substituted ester up to 25% are found.

Plasticizers

Active investigation into the mechanism of plasticizer action continues. A comprehensive review of present knowledge of the factors influencing the solubility of polymers has been provided by H. M. Spurlin.[9] The importance of solvation is assessed critically and a possible approach from acidity–basicity considerations is suggested. It has been shown by Moelter and Schweiger[10] that the heat softening of plasticized cellulose acetate is proportional to the mole fraction concentration for a large number of plasticizers; it is suggested that departure from this relationship at higher temperatures may be taken as a measure of plasticizer retentivity. In the presence of dibasic oxides the viscosity of cellulose nitrate solutions in acetone is increased rapidly and ultimately gelation occurs,[11] whereas cellulose acetate and ethyl cellulose show no such effect. This is attributed to oxidation, followed by cross-linking *via* the bivalent basic oxides. Solutions of lower concentration however suffer a lowering of viscosity, which may be due to the formation of aggregates.[12] Fractional separation by means of the ultra-centrifuge excludes chain degradation and yields enhanced molecular weights. Gels produced by means of titanium tetrachloride and ethyl titanate show a non-linear increase of cross-linking with increasing amounts of these substances and although the chemical reaction is complete within four hours the yield value of the gel continues to increase. A plasticizer compatible with nitrocellulose is obtained by reaction of butyl titanate with castor oil,[13] which is superior to castor oil, and produces harder and quicker-drying films. If however the oil be too heavily titanated the compound becomes insoluble in alcohol but soluble in hydrocarbons. Butyl titanate itself causes gelation of nitrocellulose solutions. Plasticizer action has also been investigated by means of the parallel-plate viscometer[14] and an attempt has been made to correlate plasticizer efficiency so found with that derived from plasticizer solvent-power, but without success.

A hypothetical mechanical model, by means of which the visco-elastic properties of polymer solutions may be investigated is put forward by J. D. Ferry.[15] It is clear that it is too early to offer any consistent explanation of plasticizer action which will account satisfactorily for the mass of data already collected, but there are indications that the progress so far made will eventually result in a systematic appreciation of the mechanism involved. Sebacic polyesters, unmodified and oil-modified, have a wide range of compatibility with cellulose nitrate,[16] as might be expected, they show, at high concentrations, a remarkable combination of high tensile strength and high elongation with good temperature sensitivity. The use of bis-2-diethylhexyl sebacate as a plasticizer for cellulose acetate–butyrate is claimed.[17] Vulcaprene can be employed with both acetate and nitrate provided special solvent mixtures are employed. The lacquer is opalescent and is preferably pigmented.[18] Promising results are claimed for the use of chlorinated paraffin as

plasticizer for cellulose nitrate and ethyl cellulose.[19] Pentaerythritol triacetate monostearate,[20] reaction products from olefines with formaldehyde[21] have been described, and a symposium on plasticizers[22] may be of interest.

Nitrocellulose emulsions

A promising field of investigation is opening in the use of emulsion technique. A significant saving in the cost of solvents would go far to offset the present limitations on their use. The principles of formulation are discussed by B. Campbell and A. W. Clark.[23] It is now possible to emulsify heavy-bodied high-solids lacquer with water to produce an emulsion of workable viscosity and containing two or three times as much nitrocellulose as normal lacquer.[24] Since one application of such an emulsion produces a satisfactory film, the labour cost of additional applications is also saved. Further, such procedure greatly reduces the fire risk. Early attempts with water-soluble emulsifiers produced rather poor films, owing to incompatibility with nitrocellulose. Recently a salt of a copolymer of vinyl acetate and phthalic acid (sodium polyvinyl acetate phthalate) has been patented[25] and the stability of emulsions prepared with the aid of this and similar copolymers[26] have shown excellent stability on ageing and after incorporation of pigments.[24] Prolonged storage at low temperatures did not break the emulsion provided that freezing did not occur. It has been shown that the viscosity of such emulsions depends primarily on the nature of the emulsifier[27] and is largely independent of the viscosity of the disperse phase. Low-viscosity nitrocellulose does, however, promote finer dispersions, and as viscosity is also shown to be inversely as particle size, advantage may be taken of this fact.

Testing

A direct method for the evaluation of adhesion of organic coatings to metals and non-metallic supports by means of ultrasonic vibration is proposed.[28] The film is attached to the free end of a vibrating cylinder and separation occurs when the force due to acceleration exceeds the adhesional force at the interface. The method promises to be readily applicable. Based on the foregoing investigation, it is postulated that adhesion depends on the pressure of a fluid or quasi-fluid at or near the film–metal interface.[29] It is expected that it will be possible to put forward a general picture for all types of adhesion between organic systems and their supports.

References

1 Malm, C. J. and Smith, H. L., *Ind. Eng. Chem.*, 1949, **41**, 2325
2 Eastman Kodak Co., U.S.P. 2,436,116
3 Idem, U.S.P. 2,393,794
4 McBurney, L. F., *Ind. Eng. Chem.*, 1949, **41**, 1251
5 Evans, E. F. and McBurney, L. F., ibid., 1256
6 Ibid., 1260
7 Reid, J. D. and Mazzeno, L. W., junr., ibid., 2828
8 Reid, J. D., Mazzeno, L. W., junr. and Buras, E. M., junr., ibid., 2831
9 Spurlin, H. M., *J. Polymer Sci.*, 1948, **3**, 714

[10] Moelter, G. M. and Schweiger, E., *Ind. Eng. Chem.*, 1949, **41**, 684
[11] Campbell, H. and Johnson, P., *J. Polymer Sci.*, 1948, **3**, 735
[12] Ibid., 743
[13] Kraitzer, I., McTaggart, K. and Winter, G., *J. Oil Col. Chem. Ass.*, 1948, **31**, 405
[14] Gearhart, W. M. and Kennedy, W. D., *Ind. Eng. Chem.*, 1949, **41**, 695
[15] Ferry, J. D., *J. Res. nat. Bur. Stand.*, 1948, **41**, 53
[16] Aiken, J. K. and Jones, H., *J. Oil Col. Chem. Ass.*, 1949, **32**, 150
[17] Eastman Kodak Co., U.S.P. 2,439,103
[18] White, H. G., *J. Oil Col. Chem. Ass.*, 1949, **32**, 461
[19] Wade, K. S., *Paint Oil Chem. Rev.*, 1948, **111**, No. 11, 20, 24
[20] Heydon Chem. Corpn., U.S.P. 2,441,555
[21] Standard Oil Development Co., U.S.P. 2,443,409
[22] *Ind. Eng. Chem.*, 1949, **41**, 663
[23] Campbell, B. and Clark, A. W., *Paint Manuf.*, 1948, **18**, 356
[24] Simpson, G. K. and Cavanagh, J. P., *J. Oil Col. Chem. Ass.*, 1949, **32**, 72
[25] Tattersall, H. T. and Munro, J., B.P. 552,011
[26] Lyne, R. R. and Lyne, B. P., B.P. 602,974
[27] Simpson, G. K., *J. Oil Col. Chem. Ass.*, 1949, **32**, 60
[28] Moses, S. and Witt, R. K., *Ind. Eng. Chem.*, 1949, **41**, 2334
[29] Moses, S., ibid., 2338

SOLVENTS (H. L. Howard, B.Sc., A.R.C.S., D.I.C., M.I.Chem.E., F.R.I.C.)

CONCENTRATION on production problems appears to have been the keynote during the past year, there being few developments worthy of comment. The increasing demands of the synthetic resin industry, superimposed upon the world shortage of fats, has created favourable conditions for the initiation of large-scale synthesis of glycerol. The Shell plant at Houston, Texas, based on propylene, started manufacture towards the end of 1948 and is now producing material of 99% purity.[1] The production of a new hexanetriol (1 : 2 : 6) from 2 : 6-epoxyhex-5-en-1-al, which is useful as a substitute for glycerol, is claimed[2] and so is pentane-1 : 5-diol.[3] The commercial production of 3 : 5 : 5-trimethylhexan-1-ol (nonyl alcohol) as a single substance of high purity and a large number of derivatives, likely to be of use as plasticizers, synthetic lubricants and surface-active agents are described.[4] *iso*Propenyl acetate is proposed as a unique acetylating agent, reactive with all enolizable compounds to form enol acetates in good yield. It is stated to be superior in use to keten and acetic anhydride and particularly useful where mild acetylation conditions are required.[5]

The production of limonene from gas oil by cracking in the presence of alumina–silica catalyst, followed by fractionation and treatment with sulphuric acid has been patented.[6] An interesting case of discoloration of petroleum products in a pipe-line owing to the use of a corrosion-inhibitor is reported. The spent inhibitor recovered from the pipe-line was found to be deep blue and the trouble was traced to the presence of *p*-indophenol, formed apparently by oxidation in alkaline solution of *n*-butyl-*p*-aminophenol (a common inhibitor) to *p*-nitrosophenol followed by coupling with natural phenol present in the petroleum.[7] The extension of the work on nitro compounds has passed beyond the field of solvent technology

into that of explosives, but the discovery that aluminium chloride dissolves readily in nitromethane and its homologues, forming a complex soluble in benzene, may provide a convenient method of introducing this well known catalyst into other reaction mixtures and of extending its utility.[8]

Evaporation of solvents

It has long been realized that neither the simple boiling-point nor the vapour-pressure curves afford a satisfactory guide to the evaporation of solvents from lacquer films. Investigations in this field are therefore particularly welcome. Fordyce and Simonsen[9] have examined a number of binary mixtures, selected so as to cover the three types exhibiting (*a*) minimum, (*b*) average and (*c*) maximum vapour-pressure diagrams, and have determined the change in composition as evaporation proceeds. Whereas in many of the binary mixtures good correspondence with theory was obtained, the addition of cellulose esters produced notable deviations. Retention of acetone, benzene, *cyclo*hexane and *neo*hexane is indicated, whereas toluene was retained in less amount than expected. Retention was most marked towards the end of the drying, when the film had set, as might be expected. An apparatus devised by the Shell Development Co.[10] for the determination of evaporation rate curves (*see* ANNUAL REPORTS, 1948, **33**, 397) has been shown to be suitable for routine evaporation tests but lacking in the precision necessary for more fundamental work,[11] and a more elaborate apparatus has been devised in which factorial experiments are in progress. Preliminary reports indicate that experiments in which filter paper is used as an evaporation surface can yield results markedly different from those obtained with lacquers. Retentivity due to ester gum shows up clearly and further results are awaited with interest. Systematic investigation of this problem is long overdue, but in view of the number of variables likely to influence results the greatest care is necessary in deducing the behaviour of compositions under conditions of industrial application.

Systematic correlation of azeotropic data,[12] and a method for determination of the thermodynamic consistency of equilibrium data by means of the Gibbs–Duhem equation[13] provide welcome additional checks on experimental data. The list of known azeotropes is continually being extended.[14] A table of azeotropes and non-azeotropes compiled by L. H. Horsley,[15] extending to 33 pages, supplements an earlier list by the same author[16] and should prove a boon to investigators in this field. An apparatus for the determination of a complete vapour pressure curve on one or two drops of liquid is also described.[17]

Examples of the activation of non-solvents by the addition of higher aliphatic alcohols in the absence of volatile true solvents are discussed by K. Thinius.[18]

Analysis

The estimation of traces of solvent in the air is of importance in toxicology and a new method for the determination of amyl acetate in air by absorption in ethyl alcohol, followed by reaction with *p*-dimethylaminobenzaldehyde, and capable of detecting 10 p.p.m. has been described.[19]

n-Butyl acetate does not appreciably affect results at low concentrations, and hence a means of differentiation is provided. The precautions necessary in determining water in Freon 12 and a satisfactory method for its determination within one p.p.m. are described by W. A. Pennington,[20] and a reliable and convenient method for the estimation of water in nitrogen tetroxide is now available.[21] The persistence of trichlorethylene in well water for more than four years after initial contamination is reported, and a suitable method for its estimation is described.[22] Evidence is adduced of toxicity at a concentration of 18 p.p.m.

A simplified apparatus for microhydrogenation, in which agitation is achieved magnetically, has been described,[23] as well as a micro-method for determination of unsaturation by means of iodine chloride.[24] A useful means for differentiating end-group unsaturation consists in oxidation of such groups to glycol, which is then split by means of periodic acid to form formaldehyde, distilled off and determined by chromotropic acid spectrophotometrically.[25] The colorimetric determination of nitrates and nitric esters, in the presence of stabilizers such as diphenylamine, may be effected by hydrolysing with sulphuric acid in the presence of 3 : 4-xylenol ; 6 : nitro-3 : 4-xylenol is formed, which may be estimated by steam distillation and collection in alkaline solution in which it forms a highly coloured salt.[26]

Attention is drawn to the fact that purification of ether by means of potassium permanganate and refractionation does not remove ethyl alcohol when present to the extent of 1%, and further to the fact that the presence of ethyl alcohol is not disclosed by the usual Messinger method. Its presence may, however, be demonstrated by the formation of a red coordination complex with ceric ammonium nitrate, and its removal effected by washing with 10% sodium chloride solution before drying and redistillation.[27]

References

[1] *Chem. Engng. News*, 1948, **26**, 2770 ; Sherwood, P. W., *Canad. Chem.*, 1948, **32**, 1102 ; Boyle, J. L., *Mfg. Chem.*, 1949, **20**, 327
[2] Soc. des Usines Chim. Rhône-Poulenc, B.P. 606,564
[3] Bremner, J. G. M., Starkey, F. and I.C.I. Ltd., B.P. 621,735
[4] Bruner, W. M., *Ind. Eng. Chem.*, 1949, **41**, 2860
[5] Hagemeyer, H. J., junr. and Hull, D. C., ibid., 2920
[6] Standard Oil Development Co., U.S.P. 2,388,100
[7] Sorg, L. V. and Dickey, R. E., *Ind. Eng. Chem.*, 1948, **40**, 2163
[8] Schmerling, L., ibid., 2072
[9] Fordyce, C. R. and Simonsen, D. R., ibid., 1949, **41**, 104
[10] Bradley, T. F., *Off. Dig. Fed. Paint Varn. Prod. Cl.*, 1948, No. 281, 452
[11] Rudd, H. W. and Tysall, L. A., *J. Oil Col. Chem. Ass.*, 1949, **32**, 546
[12] Othmer, D. F. and Eyck, E. H. T., junr., *Ind. Eng. Chem.*, 1949, **41**, 2897
[13] Steinhauser, H. H. and White, R. R., ibid., 2912
[14] Griswold, J. and Buford, C. B., *Ind. Eng. Chem.*, 1949, **41**, 2347 ; Griswold, J., Pao, L. C. and Winsauer, W. O., ibid., 2352 ; Frere, F. J., ibid., 2365 ; Carley, J. F. and Bertelsen, L. W., ibid., 2806 ; Wehn, W. E. and Franke, N. W., ibid., 2853 ; Alpert, N. and Elving, P. J., ibid., 2864 ; Steinhauser, H. H. and White, R. R., ibid., 2912
[15] Horsley, L. H., *Analyt. Chem.*, 1949, **21**, 831
[16] Ibid., 1947, **19**, 508
[17] Bonhurt, C. W., Althouse, P. M. and Triebold, H. O., *Ind. Eng. Chem.*, 1948, **40**, 2379

[18] Thinius, K., *Farben, Lacke, u. Anstrichstoffe*, 1948, **2**, 97, 117, 159
[19] Custance, H. M. and Higgins, M., *Analyst*, 1949, **74**, 310
[20] Pennington, W. A., *Analyt. Chem.*, 1949, **21**, 766
[21] Whitnack, G. C. and Holford, C. J., ibid., 801
[22] Lyne, F. A. and McLachlan, T., *Analyst*, 1949, **74**, 513
[23] Longenecker, W. H., *Analyt. Chem.*, 1949, **21**, 1400
[24] Phillips, Miss W. M. and Wake, W. C., *Analyst*, 1949, **74**, 306
[25] Bricker, C. E. and Roberts, K. H., *Analyt. Chem.*, 1949, **21**, 1331
[26] Holler, A. C. and Hurch, R. V., ibid., 1385
[27] Lamond, J., *Analyst*, 1949, **74**, 560

RUBBER

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Latex

THE steady increase evident over the last few years in the use of natural latex has shown no signs of slackening, the world consumption figure having risen from 25,000 tons for 1946 to over 58,000 (estimated) for 1949. U.S. consumption alone, following the removal of government restrictions in 1947, increased sharply from approximately 6000 tons in 1946 to some 30,000 tons (estimated) in 1949. It is interesting to note, however, that this increase was not made at the expense of GR-S latices, the consumption of which has been maintained at a fairly constant level.[1] Neoprene latex, however, has shown a drop in consumption from 22,200 tons in 1946 to about 3000 tons (estimated) in 1949.

With regard to the future position world production capacity has been estimated at 100,000 tons dry weight which could probably be increased to 150,000 tons for 1950 under planned expansion.[2] On this basis, with U.S. consumption at the 30,000 tons a year level, and a total world consumption estimated between 50,000 to 60,000 tons, it would appear that supply should be in excess of demand for some time to come.

This position is likely to stimulate research and development work both in the examination of the raw material with a view to improving its inherent properties and also in attempts to expand the field of application of the finished product. Marked successes in the latter direction have been achieved over the last two years especially in regard to dipped goods, treatment of fibrous materials, adhesives and, above all, foamed latex for upholstery purposes. Some further comment will be made on this later.

In the more fundamental research work on latex, investigations have been carried out on the formation of rubber in *Hevea brasiliensis*. The literature on the subject has been reviewed and the formation of rubber considered as part of the metabolism of the tree.[3] Primary formation in new tissues and secondary formation occurring in the bark on tapping are differentiated and the analysis of seedlings is stated to indicate that rubber is formed as a by-product of growth metabolism. It is also suggested that the yield capacity of a tree can be predicted from the rubber content of the leaves of the seedling. The metabolism of the rubber tree was also the subject of a paper read at the International Congress on Biochemistry.[4] According to the author the synthesis of latex takes place mainly in the green parts of the plant and principally direct from carbon dioxide. The rubber exists initially in liquid form as a low polymer of isoprene and is circulated through the plant as a high-dispersed oil-in-water emulsion. Polymerization, which probably takes place mainly in the latex vessels, results in the formation of the solid phase, the solid rubber being deposited in the plant. Investigations on the biosynthesis

of rubber are also being carried out at Cornell University under the sponsorship of the U.S. Office of Rubber Reserve, Reconstruction Finance Corporation, and an interim report has been issued[5] defining the object of the work as the determination of the particular organic substances that serve as immediate precursors of the isoprene units that are converted by various plants into polymeric isoprenoid structures. Such information, it is hoped, may serve as a basis for investigating the intimate mechanism of the natural polymerization process. It is probable that simple molecules of carbohydrate origin, such as acetic or pyruvic acids, are the starting materials for natural synthesis of isoprenoid structures and the present work is based on the assumption that pyruvic acid and acetone undergo condensation to furnish a C_6 hydroxy-acid which leads to an unsaturated C_5 alcohol or a saturated C_5 glycol that plays a significant role in isoprenoid synthesis.

In a microscopic examination of the *Hevea* latex complex, G. E. van Gils has fractionated fresh, non-ammoniated, undilute latex into yellow and white fractions. The rubber particles appear as a grey glittering mass interspersed with clear, irregular-shaped lutoids. The lutoids, which are an important cause of variability in the rubber, consist of viscous gelatinous masses with varying form and shape depending on the tree and the time of examination after tapping.[6] Only when latex is centrifuged and all lutoids are assembled at the bottom of the tube is the yellow colour discernible. The Frey-Wyssling particles separate as a thin layer on top of the lutoids after centrifuging the latex and they rapidly disperse in the white fraction. Investigations are being carried out by the Netherlands Indies Rubber Research Institute on the chemical differences between the Frey-Wyssling globules and the lutoids.[7]

A number of processes have been patented during the year involving the fractionating of natural rubber latices into white and yellow fractions. In one case, for example, the p_H is adjusted to a value of 6·0 –8·5 with the aid of ammonia and a small proportion of a solution of a salt with a univalent cation added. Both the yellow and the white fractions are obtained in a stable fluid state, separation being carried out in the usual manner.[8] An addition of an aqueous solution of a magnesium salt has also been recommended after the adjustment of the p_H value to 6·8–8·0. After separation, a rubber can be manufactured from both the fractions, the yellow fraction giving a yellow crêpe and the white fraction a lighter crêpe.[9]

The effect of surface tension on stability has been examined by A. S. C. Lawrence[10] who concludes that although surface tension determines the work to be done in emulsification it appears to play no part in determining stability. It is also suggested that the anomalous viscosity of some soap-stabilized emulsions is due to the rigidity of the soap monolayer. No emulsion of a hydrophobic solution is considered likely to have an absolute stability. The stabilizing power of soap solutions in latex in the presence of inorganic salts and some amino-acids has been reviewed by K. W. Gardiner[11] who states that the ultimate stability of blends of soap-stabilized latices will be dependent chiefly upon the degree of interaction occurring between the stabilizing media characteristic of each latex. A study has also been made of the emulsion stability behaviour of a purified

natural latex in which the proportions of several potentially reactive ingredients representative of each stabilizing system have been systematically varied, the changes in stability being explained on the basis of salt effects and the possible association of one of the soap hydrolysates employed with certain amino-acids. The actual enhancement of emulsion stability resulting from the association of a stoichiometric acid soap with the amino-acids has also been demonstrated.[11]

In a paper dealing with the part played by surface-active agents in the latex industry, the use not only of fatty acid soaps but of other anionic agents such as aliphatic and aromatic sulphonates has been described in relation to the stabilization and emulsification of latex.[12] The use of cationic soaps to reverse the charge of latex, giving it an increased affinity for textile fibres, is also discussed in the same paper.

The stability of latex is greatly influenced by the presence of small quantities of metallic salts, such as salts of potassium, sodium, iron, magnesium and calcium, and a colorimetric microtitration method has now been developed to study the behaviour of these metallic ions in latex.[13] A mechanical stability test has also been described as a rapid, simple method of estimating the colloidal stability and quality of *Hevea* latex.[14]

The best methods of storing and handling latex have been reviewed by W. H. Stevens[15] who discusses the use of various materials such as bitumen, Prodor-Glas, polyvinyl chloride, etc. for the lining of latex-containing equipment, and the conditioning and packing of latex have been considered by R. Cosset[16] in relation to hygienic tapping, precautions after tapping, collection, cleaning, transport and the use of tanks.

The theoretical aspects of the problem of latex concentration have been dealt with by I. Sibiriakoff[17] who describes the main methods of latex concentration by the elimination of water and by centrifuging, creaming or electro-decantation. Instability factors and their effect on the behaviour of the latex are studied in relation to the methods of concentration. Centrifuging is considered the best method on the grounds of speed and its possible application to all latices. Creaming is considered the next in value, the electrodecantation method being, in the opinion of this worker, the least useful because of the special conditions involved which harm the stability of the latex.

Among the creaming agents mentioned in the year's literature is glucomannan, a colloidal substance derived from *Amorphopallus* corms. The use of this material is stated to render centrifuging unnecessary, thus eliminating capital expenditure on expensive equipment, but its application at present is limited to certain types of latex only.[18] The use of alginates for creaming has been freed this year from patent protection and details have been published[19] of the creaming technique used and its advantages over the method of using K meal.

Experiments carried out on the effects of various thickeners on natural and synthetic latices have been described by L. H. Silvernail.[20] The thickeners used included methyl cellulose, sodium carboxymethyl cellulose and water-soluble polyacrylate resin, and the experiments were intended to show how different thickeners are more efficient in certain types of latex.

Developments in the heat sensitization of latex have been reviewed by C. M. Blow[21] who deals mainly with the French method by which the effect is produced by degradation of a protein protective stabilizer and the addition of zinc oxide, and the German method using polyvinyl methyl ether, which is a stabilizer at room temperature but not at elevated temperatures owing to its insolubility. A Canadian patent[22] claims that latex can be made to coagulate solely by heating to about 85° c. with the addition of a colloidal suspension of zinc oxide in the proportion 2–4% by weight of the rubber present in the latex and allowing the mixture to mature for several days; M. Hooreman and F. Lepetit[23] have shown that *Hevea* latex, treated with proteases of the trypsin group (pancreatic extract from pork) and zinc oxide, can be coagulated by heating on a water bath at 50–70° c., whereas untreated latex is stable under these conditions. Continuing his studies of the trypsin treatment and the heat sensization of latex, F. Lepetit has presented evidence to show that the degradation of ammoniated latex alters its stabilizing constituents, especially the proteins, leading to the formation of amino-acids which remain in the serum. These acid products, together with the ammonia in the latex and the zinc oxide form zinc–ammonium complexes, the coagulating power of which is increased by the decreased stability of the rubber particles.[24]

The application of high-frequency dielectric-heating in the drying of latex was mentioned in last year's review. Details of a process have now been patented[25] in which latex is subjected intermittently to an alternating electric field of radio-frequency. The latex compositions may be passed between pairs of electrodes to which an alternating potential is continuously applied and the intermittency may be effected by periodically moving one electrode away from the other so that the field becomes negligible.

At the beginning of this section attention was drawn to the marked increase in the consumption of latex, especially in the production of latex foam for upholstery, and it has even been suggested that the use of rubber for this purpose in America may become second only in importance to that of tyres.[26] The references on foamed latex that have appeared in the year's literature are so extensive that only a short and somewhat arbitrary selection can be made in the available space.

The early history of latex foam has been reviewed by R. F. McKay,[27] and P. P. Crisp[28] has surveyed the various uses of foamed latex both during the war and for the civilian market. Mattresses, padding for rooms for mental hospitals, dress models, pads for clothing, surgical articles and shoe soles are among the many applications named. The physical evaluation of latex sponge has been dealt with by F. S. Conant and L. A. Wohler[29] who describe testing methods for the evaluation of tensile strength, compression modulus and fatigue resistance. The relationship established by compression modulus–% deflection curves appears to imply that the principal mechanism of compression is a buckling of the cell-wall remnants. The effects of density on the physical properties of foamed *Hevea*, neoprene and 50 *Hevea*/50 GR-S latices are given and a physical basis is postulated for the greater comfort of sponge-rubber cushions as compared with coiled steel spring cushions.

A number of patents have been taken out covering new mechanisms for frothing. One apparatus,[30] which is said to facilitate the uniform dispersion of gas in the latex, consists of concentrically arranged imperforate members of cylindrical form with alternate members mounted for rotation, the whole being contained in a chamber into which gas and latex are admitted. Another mechanism consists of two or more frothing chambers in series and connected through restricted openings each arranged to connect a froth-containing part of an earlier chamber to a liquid-containing part of the next chamber. Solidification of the froth may be produced by passing it between electrodes.[31] Apparatus has also been described[32] by which foamed latex can be continuously frothed, poured on to an endless belt which carries it under a doctor blade, gelled, vulcanized and dried continuously. A further continuous method of producing sponge necessitates the unvulcanized material being passed through a high-frequency electrostatic field on a layer of finely divided dielectrical material[33] and a continuous frothing method has also been patented[34] wherein large bubbles of air are made smaller in successive stages by means of a number of beaters, operating at progressively increased speeds.

A stronger and more uniform sponge has been claimed for a method by which latex foam is first frozen insufficiently to cause coagulation and then treated with a coagulant such as ethyl alcohol or an acid or by gas such as sulphur dioxide or carbon dioxide[35] and another method has been described[36] by which a soap is formed *in situ* within a large quantity of an aqueous vehicle by the addition of a fatty acid and a saponifying base and simultaneously stirred at high speed. An oily softening agent, fillers and other compounding ingredients are added and the latex dispersed in the mixture.

The danger of the collapse of the foam structure during the heating of gelled latex foam has been counteracted by a process in which no acid-generating gelling agent is used, the main factors involved being zinc oxide, an alkali soap of a soap-forming monocarboxylic acid having 12–20 carbon atoms and an electrolyte which yields alkali metal cations to cause delayed gelation of the soap.[37] A related patent[38] involves the use of a latex foam containing zinc oxide, a sequestering agent for polyvalent zinc ions, an alkylated phenyl monoether of polyethylene glycol and a slightly soluble salt of fluosilicic acid. Examples of the sequestering agent include an alkali carbonate, borate, phosphate, sulphite, oxalate, ferrocyanide, ferricyanide or chromate.

Among the other latex foam processes covered by the patent literature of the period under review, mention may be made of the use of ammonium fluozirconate as a delayed coagulant[39] and the addition of a small quantity of a fluotitanic acid salt to alkaline dispersions as a control on gelation time.[40]

A few miscellaneous applications of latex may be briefly noted here. Road surfacing experiments in France using latex and bitumen emulsion have been reviewed[41] and a flooring composition has been patented consisting of latex, cement powder and coir dust.[42] The use of Positex has been discussed in relation to light-weight woven cotton belting[43] and W. H. Stevens[44] has reviewed the history and present manufacturing methods of latex thread. Recent research work on corrosion has directed

attention towards the use of latex treated with sodium benzoate as an anti-corrosion coating.[45] Small articles can be dipped in the treated latex and larger articles coated by spraying. A decided advantage of this coating is that it can readily be removed when no longer required.

Raw rubber

The interest in the preparation of purified rubber, mentioned in last year's Report, has continued during the period under review and the London Advisory Committee for Rubber Research (Ceylon and Malaya) in their Annual Report for 1948 have outlined an attempt to improve the purification process. According to this method the latex is treated with soap and repeatedly creamed by electro-decantation in a series of Perspex cells separated by cellulose acetate films. The reports also comments on the use of antioxidants to counteract the tendency of purified rubber to oxidize rapidly. Alkaline pyrogallol, the first anti-oxidant tried, was shown to have a hardening effect on the rubber and to retard vulcanization.[46]

A consideration of the various methods of purifying *Hevea* rubber has led to the view that whereas the alkali treatment appears to be the most satisfactory, the drastic chemical treatment involved might adversely affect the molecular structure of the rubber hydrocarbon. A new method has been proposed[47] by which the latex is treated with ammonium oleate which displaces the proteins from the surface of the rubber particles. The displaced proteins, along with other non-rubber substances present in the serum, are then removed by repeated creaming with ammonium alginate. A rubber has been prepared in this way with a rubber hydrocarbon of about 99·4% purity. The same worker has fractionated purified and unpurified rubber by treatment with *n*-hexane containing 10% methanol.[48] It was found that with progressive extraction 70% of the purified rubber was dissolved as compared with 50% of the unpurified rubber. The molecular weight of the purified rubber ranged from 127,000 to 248,000 (1st to 10th fractions) and the unpurified rubber from 170,000 to 261,000 (1st to 10th fractions). A large concentration of nitrogen and ash was found in the undissolved portions. A study of the behaviour of different fractions of purified and unpurified rubbers during vulcanization has been made[49] and it was noted that in a rubber–sulphur mix the first fraction of the purified rubber did not give a good vulcanizate, although most of the other fractions gave a higher combined sulphur figure than the corresponding fractions of unpurified rubber. In connexion with the rate of cure of purified rubbers, H. P. Stevens[50] has referred to an early paper of his dating back to 1912 ; in it he showed that rubber purified by diffusion, if cured in a pure gum type of mix, is characterized by slow curing properties owing, it is stated, to the elimination of the natural accelerator which can be isolated as a phosphotungstate.

The revival of interest in powdered rubber has been noted by T. R. Dawson[51] who outlines the methods of production for 'Pulvatex' and the newer 'Mealorub' types. 'Pulvatex' can be made by the Stam process in which a protective colloid is added to the latex and the mixture sprayed by a centrifugal pump into a current of hot air, or by the de Schepper method by which the latex is sprayed on to a heated endless belt and

passed through a chamber at 90–120° C. The 'Mealorub' powder is produced from ammoniated latex to which are added sulphur, zinc oxide, Vulcafor SDC and Captax, the mixture being heated to 80° C. for 2½ hours and then coagulated with formic acid. The product has been used for road surfacing and for protective coatings; it can also be cold-cured or moulded and heat-cured if vulcanization agents are included.

Further details have also appeared in the patent literature of processes for the production of crumb rubber from latex. According to one method,[52] latex is added to a solution containing 0·25–5% by weight of a water-soluble zinc salt (e.g. zinc chloride) and ammonium hydroxide in the proportion of 1·5 to 4 mol. ammonium hydroxide per mol. of zinc salt. By another process,[53] frozen coagulated latex particles are heated to above the freezing point of the serum and the temperature maintained to bring about the syneresis of the serum to the outside of the particles. The serum is then re-frozen and mechanically removed and the particles dried to form a crumb rubber.

As in previous years, a considerable amount of attention has been given to the phenomenon of the oxidation of rubber. Rubber, because of its unsaturation, is degraded by atmospheric oxygen, a small degree of oxidation being sufficient to destroy its rubber-like characteristics. The oxidation process is very complicated, involving several reactions each of which is influenced differently by varying conditions. Some of these reactions have been investigated by A. M. Neale and J. R. Vincent[54] with special reference to the effects of, for example, a given material on the rubber, chemicals on mill breakdown, different antioxidants on a similar stock, combinations of metal catalysts, oxygen pressure on the temperature coefficient of the oxidation, temperature on the amount of oxygen required for degradation, and different ageing conditions. Chemical changes in elastomers and antioxidants have also been studied by J. O. Cole[55] who reviews the changes which occur during thermal and photochemical oxidation. As definite conclusions are difficult to obtain by direct experimentation with polymers, the approach taken by this worker involves the investigation of the oxidation products of low molecular weight olefines closely related to the polymer in chemical structure. Of the experimental methods applicable to the direct study of polymer oxidation products, infra-red methods are among the most promising. The infra-red absorption spectra of elastomers undergo marked changes as the result of oxidation, and the interpretation of these changes is discussed. Antioxidant consumption during natural and artificial ageing is also demonstrated by analytical methods. A kinetic investigation of the photochemical oxidation of certain non-conjugated olefines has been carried out by L. Bateman and G. Gee,[56] who have found that photo-oxidation of *cyclo*hexane, 1-methyl*cyclo*hexane, dihydromyrcene and ethyl linoleate proceeds by a chain-reaction mechanism in which the initiation reaction is the photolytic generation of free radicals and the propagation and termination reactions are those recognized in analagous oxidations catalysed differently. It is established that the dominant initiation process is the photolysis of the olefine hydroperoxide. When the light absorption is very strong it is shown that the basic kinetics are specifically modified. In continuing their investigations on the basis

of the reaction mechanism established above, the same authors have analysed the changes in photo-oxidation observed in intermittent light when a rate contribution is made by a simultaneous dark reaction.[57] The velocity coefficients of the rate controlling propagation and termination reactions have been separately evaluated for *cyclo*hexane, 1-methyl-*cyclo*hexane, dihydromyrcene and ethyl linoleate. The authors discuss the significance of the results in interpreting the finer details of the oxidation mechanism and compare the numerical values with similar data reported for polymerization systems.

An ordered presentation of the literature on the kinetics of olefine oxidation has been made by J. L. Bolland.[58] After discussing the chemical nature of oxidation products, the influence of olefinic structure on propagation processes, peroxide formation and decomposition products and the oxidation of peroxide-free olefines, the author concludes that the oxidation chains are initiated by the unimolecular dissociation of benzoyl peroxide into radicals which in turn lead to the production of *R*-radicals, *R*· representing the radical produced by the removal of an α-methylene hydrogen atom.

The mechanism of chain propagation in the oxidation of polyisoprenes has been discussed by J. L. Bolland and P. Ten Have[59] as part of their kinetic studies in the chemistry of rubber and related materials. The interaction of squalene with oxygen in the presence of benzoyl peroxide both in the presence and absence of hydroquinone has been described and the mechanism by which oxidation chains are propagated and terminated in these systems shown to be analogous to that already determined for the oxidation of mono-olefines and 1 : 4-dienes. An investigation into the identity of the chain propagation reactions in the oxidation of polyprenes is included in the same paper.

The application of mathematical principles to the rheological examination of rubber has been studied by H. Hencky[60] who points out that, to increase the efficiency of the mathematical theory of elasticity, classical kinematics must be expanded and the equations of equilibrium extended so as to abolish some existing contradictions. The author proposes a synthesis of elasticity and hydrodynamics and illustrates by concrete examples the general equations of rheology that are deduced. In a further rheological examination of rubber, factors such as stress–strain curves, tearing strengths and plastic flow under constant load have been measured on test strips of various rubbers, including raw rubber, at temperatures from $-80°$ C. to room temperature and the flow limit, alteration in translucency and decrease in tensile strength examined.[61] Flow effects were found to be much greater at low temperature and a small elastic after-effect was observed. A general similarity was also noted in the results for natural and synthetic rubber.

The plasticity of rubber is one of the subjects dealt with in the Annual Report for 1948 of the London Advisory Committee for Rubber Research, mentioned at the beginning of this section.[46] Investigations carried out during 1948 indicate that the effect of chemical softeners is in some circumstances reversible. The most effective hardening agents are stated to be those containing two amino groups substituted in different positions in one or more benzene rings, e.g. benzidine. The sol fraction

has been found to be much more sensitive than the gel fraction to hardening and softening agents. The report also comments on the fact that oxygen appears to play a significant part in the hardening and softening of rubber. A series of Japanese papers have described studies on the plasticity of rubber from the point of view of plasticity index and the effect of the magnitude of stress in the measurement of plasticity, and the temperature coefficient of plasticity has also been investigated, the results obtained leading to the assumption that the molecules themselves are not flexible and when they are of high molecular weight they flow in large blocks.[62]

The structural viscosity of rubber has been studied mathematically by S. Kambara[63] who derives a new formula from a combination of Ostwald's formula for structural viscosity and Staudinger and Heuer's formula for relative viscosity and degree of polymerization. Measurements of the viscosity of solutions of natural rubber and synthetics have been made and the degree of polymerization calculated by means of the new formula. Modern instruments designed for the measurement of viscosity have been reviewed[64] in connexion with the analysis and production control of highly viscous materials. The Steiner viscometer is particularly suitable for plotting viscosity–temperature curves and the plunger rheometer based on the Gardner mobilometer enables curves between shear stress and viscosity to be plotted easily. The use of a continuously indicating viscometer together with a viscometer for controlling a process automaticaally for a constant viscosity using radio-control is mentioned in the same paper, and N. A. de Bruyne[65] has described the Techne instrument which is designed for the rapid viscosity measurement of thick, sticky liquids.

The application of infra-red spectroscopy to the examination and testing of rubber has increased considerably in importance over the last few years. An article by J. Mann was noted in last year's Report and the same author has now published a general outline of the experimental methods employed in quantitative and qualitative analysis and in structure diagnosis on molecules.[66] Each organic radical has a characteristic frequency which enables chemical changes in polymers to be followed, and although the use of a spectrometer may not be economic as a control instrument in service testing, its use is throwing much light on problems relating to oxidation, sunlight stiffening, identification of bloom and the mechanization of accelerators. Recent developments in technique have been discussed by G. B. B. M. Sutherland who describes some of the detectors used and gives a brief account of the use of a polarized beam of radiation for examining the spectra of crystals.[67,68,69] Single- and double-beam instruments, prism materials, and infra-red analysers have been studied by F. R. Cropper and A. Hamer[70] and an illustrated description has been given[71] of the spectrometer used by the Research Association of British Rubber Manufacturers at Croydon. Determinations of oxygenated and olefine compound types have been made by infra-red spectroscopy[72] and the infra-red absorption spectra of a series of polymers including rubber have been studied at liquid helium temperatures by G. W. King, R. M. Hainer and H. O. McMahon[73] who report that no unusual changes occur on cooling which considerably alter the absorption. There is some

sharpening and improvement in resolution, but the width of most bands in polymers remains wide.

Among the papers dealing with the examination of rubber from a more general point of view mention may be made of the 4th Foundation Lecture of the Institution of the Rubber Industry in which the Director of the British Rubber Producers' Research Association surveyed recent advances in polymer science in the light of possible improvements in rubber technology.[74] An outline of the statistical theory of plasticity is given and methods of processing raw rubber reviewed. Lines for further study are also indicated, the methods of polymer science being suggested as offering the best prospect of advance.

The structure and composition of elastic colloids have been investigated by E. A. Hauser[75] who states that extensive research supports the two-phase theory of the structure of rubber and offers visual evidence that all colloids exhibiting elasticity are of a two-phase composition, and an account has been given[76] of the methods which have proved successful in elucidating the molecular structure of natural rubber. The rubber molecule appears to consist of up to about 5000 isoprene units linked together into a long chain in the *cis* relationship and local crystallizations can occur along the length of the molecule. The behaviour of high-polymer molecules in solution has been studied by A. R. Miller[77,78] who indicates the necessity of developing a new methematical theory which will take account of the complex action between polymer and solvent, and formulæ are given for the free energy of a monomer–polymer system together with equations for vapour pressure. The author states that there is evidence to show that in dilute solution the polymer molecules tend to segregate, coil up and form clusters. If allowance is made for this a theoretical curve can be obtained which corresponds to the experimental curve for entropy of dilution *versus* concentration.

Rubber derivatives and synthetic derivatives

The advantageous qualities of rubber derivatives, particularly those of chlorinated rubber, continue to find fresh applications and promote developments in the protective coating field. Five paints designed for extreme corrosion resistance, for example, have been examined and the results indicate that formulations based on vinyl resins and chlorinated rubber gave the best resistance against chemical attack. Chlorinated rubber has also been reported as especially useful in coating concrete floors and tanks.[79] J. B. Martin has examined the most suitable plasticizer for use in this type of coating without which the film is insufficiently flexible. Chlorinated paraffin appears to be the best for maintaining good chemical resistance, and alkyd resin or phenolic varnish for maintaining adhesion, gloss and toughness.[80] The preparation of rubber hydrochloride from latex has been described in which the latex is swollen with benzene and shaken with ethyl acetate containing 15 to 25% hydrochloric acid. The highly polymerized hydrochloride is obtained in the form of a fine powder.[81]

T. R. Dawson has given a detailed description of the preparation, properties, and uses of the principal rubber derivatives including cyclized rubber, chlorinated rubber and rubber hydrochloride. Other derivatives

of less practical value are treated more briefly, e.g. oxidized rubber, hydrogenated rubber, fluorinated rubber, brominated rubber and addition products with maleic anhydride and acrylonitrile.[82] Some interesting condensation products of rubber with formaldehyde have been developed for use as adhesives and for the surface hardening of rubber articles.[83]

The great interest in synthetic rubber has been focused on the rapidly increasing production of 'cold' GR-S in the U.S.A. and natural rubber has been suggested as an alternative source of hydrocarbon in place of petroleum.[84] Harvey I. Firestone, junr. predicts that manufacturers will probably use 'cold' rubber on a voluntary basis in place of natural rubber.[85] A. O'Neill, at the 6th International Rubber Study Conference, said that rubber growers were surprised and somewhat 'panicky' at the progress in the man-made rubber world.[86] This view may be emphasized by the statement of the Rubber Growers Association that the plantation industry contemplates spending considerable sums of money on propaganda in the U.S.A.[87]

R. P. Dinsmore, on the other hand, is more cautious in his assessment of the position and discusses the requirements with particular reference to the stocking of natural rubber in anticipation of possible future stoppage of supplies. He points out that, although 'cold' rubber has shown better tread wear than natural rubber, some aspects have not been fully investigated. These include hot-weather testing and skidding under wet conditions.[88]

A very frank paper by J. H. Fielding reviews the properties of 'cold' rubber particularly for tyres ; it is considered an improvement over normal GR-S in most of its laboratory properties. It is superior to natural rubber in wear but inferior to it in most other properties. It was not anticipated that 'cold' rubber would be used in larger tyres or in the casings of smaller tyres. It was not considered the equal of natural rubber and could not be expected to do away with the need for natural rubber.[89]

The increasing availability of 'cold' rubber with further reductions in manufacturing costs can be expected in the near future when the plants have been converted to a continuous polymerization process. Progress in this direction is described in a communication from the Government Laboratories, Akron University, which deals with the pilot plant work for the continuous process at 41° F.[90]

During the year under review, an increasing number of papers have appeared dealing with the compounding and factory processing of the cold polymers. A long and critical study by I. Drogin and co-workers[91] contains extensive data and examines five low-temperature GR-S rubbers. Natural rubber and GR-S were used as controls. The author's main conclusions are that the 41° F. rubber (X485) is generally superior to GR-S 10 in processing characteristics and vulcanized properties. Compared with natural rubber the only important advantage of X485 is its higher abrasion resistance. The 14° F. and 0° F. rubbers show some advantages over GR-S 10 but are inferior in two important respects : they have a slower rate of extrusion and lower abrasion resistance.

Of the reinforcing blacks, Kosmos 60 imparts the best processing characteristics, but the black that gives the best vulcanized physical

properties varies with the characteristics required. Incidentally, the author states that one-half the total GR-S production is to be converted to 41° F. during 1949, indicating the view that this rubber is superior to standard GR-S.

A number of reports dealing with power consumption during compounding of cold GR-S have appeared but the evidence brought forward seems rather conflicting. It is stated that power consumption is greatly influenced by type of black used[92] and that preliminary plasticization in a Gordon Plasticator does not reduce power consumption. Overloads of 50–60% were experienced with frequent stalling of the Banbury motor. D. M. Sheppard,[93] on the contrary, states that the Banbury power requirements of 'cold' rubber are a 'little' higher than that of standard GR-S and that normal compounding practice as used for standard GR-S can be used with little change except for a small increase in accelerator content. H. C. Steffen[94] shows the value of VFF black in this connexion and states that when using this black, the processing is no more difficult than when using standard GR-S and that large quantities of softener are unnecessary. Best results are stated to be obtained under high temperature conditions (about 375° F.) which permit high speed mixing. So processed, the VFF 'cold rubber' tyre gave 5% better road wear than a tyre made from a stock of similar Mooney value containing fine-particle oil black (high-abrasion furnace type).

The use of VFF blacks on the vulcanized rubber is stated[95] to increase tyre tread wear by 10–25% compared with standard GR-S with less tendency for tread cracking; traction on wet roads is 10% better than natural rubber. These authors also declare that in processing and general characteristics 'cold' rubber compares favourably with GR-S and that physical properties have, in general, been intermediate between GR-S and natural rubber.

Attention is drawn to the difficulties of processing low-temperature polymers[96] owing to the lack of breakdown when mastication is carried out under normal conditions. Increasing the time of breakdown, particularly at high temperatures, causes a toughening which the use of a small amount of aromatic mercaptan will not overcome. The best softening is obtained by using 1% of mercaptan and masticating for 5 min. below 177° C. The addition of a diamino antioxidant may be advantageous.

The development of fast, low-temperature recipes for polymerization resulted from a great concentration of effort to solve the problems of reaction initiation. At first it was assumed that faster recipes could always be conducted at lower temperatures, but in one instance it was found that this did not occur.

The recipe must, therefore, be developed by experiments at the actual temperature at which it is to be used. A summary of the progress made over the last 10 years, including details of many practical recipes, has been given.[97] In this field an investigation has also been reported on the mechanism of the Redox low-temperature polymerization system. It is found that ferrous iron, solubilized in the oil phase as the stearate, promotes the decomposition of benzoyl peroxide into free radicals capable of initiating polymerization, and an essential reason for the use of sodium

stearate, apart from its emulsifying properties, is its ability to render the iron salts soluble.[98] Further information on the role of the iron complex has been published. An active catalyst is formed by interaction with ethylene dinitrilo tetraacetic acid and its structure has been discussed. Various other organic iron complexes have also been the subject of experiment, e.g. salicylate, citrate and lactate, and have proved to be effective activators.[99] A systematic study has been made on the effect of oxygen on the rate of polymerization. The inhibiting action of oxygen has previously been demonstrated by I. M. Kalthoff and others and further work has been undertaken to check the sensitivity of different recipes to the presence of oxygen. Tentative conclusions suggest that (1) only systems containing ferrous sulphate are markedly sensitive (2) that the type of system, rather than the temperature, seems to determine the sensitivity. Since ferrous sulphate containing Redox formulations are used for the production of 'cold' GR-S, it is recommended that oxygen should be excluded from the system at all times.[100] The effects of the polymerization temperature on the structure of the resulting polymer has been reviewed. Unsaturation is but little affected but reduction of temperature increases the structural regularity and gives less low molecular weight fractions and less branching. The introduction of styrene to polybutadiene retards crystallization and with 20% styrene even a $-20°$ c. polymer is amorphous.[101]

Although so much interest has been displayed during the year in connexion with low-temperature polymerization, the development of other synthetic polymers has not been neglected. The properties and processing characteristics of Hycar PA21, formerly Lactoprene EV, have been mentioned in several papers. Hycar PA21 is a copolymer of 95% ethyl acrylate and 5% 2-chloroethyl vinyl ether and its vulcanizates have an acceptable flex life and resistance to high temperature, oils, oxidation, and sunlight.[102] Several modifications of Hycar PA21 designed for easier processing have been made available, and are stated to be not as good as silicone rubbers in heat resistance, but superior to silicone rubbers in physical properties. Data are available of the properties of all polymers in this series.[103]

The acrylonitrile type of polymer is finding increasing applications in combination with other types of polymer. A comprehensive study of mixtures of nitrile rubbers with P.V.C. and polyvinylidene chloride has been published.[104] Mixtures with phenolic resins have been investigated and their application as adhesives reported on. They are recommended for shoe-making and fibreboard work.[105]

Butyl rubber continues to be popular on account of its low gas-permeability, and, despite serious import difficulties, manufacturers in Western Europe have been reported as having converted completely to Butyl for car inner tubes.[106] Confidential war-time information on the vulcanizing of butyl has now been released for open publication. Vulcanization is accomplished by means of *p*-dinitrobenzene in the presence of an oxidizing agent, e.g. lead peroxide; the activity of the curing agent can be restrained by converting it into an aromatic ester. Details of many materials tried as scorch retarders are listed, the most satisfactory being octadecylamine.[107] Butyl, in conjunction with ebonite,

has been recommended as a plant lining to withstand the action of hot fatty acids.[108]

A new type of neoprene, type RN, has been introduced which is claimed to have all the properties of general purpose neoprene in addition to a high degree of flexibility at Arctic temperatures.[109] Another improved neoprene, type W, has a more uniform molecular weight distribution than any other neoprene. It contains no sulphur, thiuram disulphide, or other compounds capable of decomposing to give either free sulphur or a vulcanization accelerator, and it is claimed to have superior storage stability, improved processing characteristics and favourable response to a variety of vulcanizing systems. The work presented in this paper[110] shows that both with regard to the vulcanizing systems used and the physical properties of the resulting vulcanizate, neoprene type W is more like natural rubber than any of the other neoprenes. A further neoprene, type RT, is claimed to possess markedly improved retention of building tack and flexibility.[111]

Development work on fluoroprene suggests that this material, although not yet commercially available, may soon be a competitor in a similar field to neoprene. Freeze- and oil-resistance are stated to be good. Unlike chloroprene, it copolymerizes freely with other monomers to yields rubbers with interesting characteristics. Copolymers with styrene exhibit good electrical properties and copolymers with acrylonitrile are reported to have outstanding oil resistance and high tensile strength.[112]

Prof. M. Stacey, of Birmingham University, has contributed an interesting and informative review of the development of fluorine chemistry during the war, with particular reference to the fluorocarbons.[113]

The unique properties of the organic silicon compounds continues to find increasing application over a very wide field. Silicone rubber, the properties of which are inherent in its chemical structure, has been developed and its improved properties have been reported. These include (1) increased tensile strength and elongation; (2) ability to withstand lower temperatures; (3) greatly reduced compression set; and (4) the property of being self-extinguishing when the kindling flame is removed. In general, only one of these improvements has been incorporated in a single formula, but some of the newer stocks possess two or more of these desirable features.[114]

Their use in the paint and electrical industries has been extended as their solubility in aromatic solvents and heat resistance are especially valuable.[115] When incorporated into a film for wire insulation, they are claimed to withstand temperatures up to 180° C.[116]

An important application of dimethyl silicones for de-webbing latices has been patented.[117] Another development of interest to a variety of industries is the application of rolls covered with silicone rubber. The covers are claimed to remain soft and workable from − 100° to + 500° F., thus permitting the processing of many plastics, metals and fabrics.[118] A novel use for a silicone water-repellant will be welcomed by many workers with latex. It is reported that a simple application of the diluted silicone to glass dishes used for handling latex will prevent the adherence of latex to the glass and reduce the dishwashing routine to a few minutes rinsing in water.[119] A review has been published of the

present position of silicones with particular reference to the work done in the Chemical Research Laboratory at Teddington. Points considered include nomenclature, direct syntheses from silicon, nature of the chlorosilanes, control of chain length and cross-linking and practical properties.[120]

Compounding materials

Interest has been stimulated by the announcements made as to the progress of carbon black manufacture in U.K. Work on the Avonmouth site commenced in May and the plant is expected to be in operation for the production of Phillblack and Phillblack 0 during the latter half of 1950.[121]

The first bulk production of furnace type black at Swansea was announced during the year using Ayrshire shale oil and imported petroleum. The Merseyside factory is expected to produce up to 10,000 tons of furnace type per annum within the next two years, making the total planned output for this country about 30,000 tons when all plants are in full operation.

A patent for a continuous furnace process claims to produce a product which is superior to channel black and to give a yield up to 50% of the carbon content of the gas. The type of black obtained can be varied by the operating conditions, so that either soft, intermediate or hard blacks can be produced. By this means continuous operation is possible whatever the current demands of the market.[122]

Several patents typify the main approach to the problem of incorporating black and other pigments into the rubber while the latter is in the emulsion stages. The production of the polymer in which a stated amount of black is already incorporated can prove a very attractive proposition to the rubber manufacturer, who is thus saved the expense of conducting the dirtiest mixing operation in his own factory. Carbon black is combined with an aqueous dispersion of the polymer, coagulated, and the solids drained free of liquid. The drained wet solids are then extruded through an opening not exceeding $\frac{3}{4}$ in. maximum dimension to cause smearing of the agglomerated carbon black particles through the mixture. It is claimed that the black particle is thus completely enclosed in rubber and that, therefore, there is no black smear when handled.[123]

C. M. Blow describes a method for making dustless black by wetting out the black with a cationic or anionic soap before adding it to the latex and coagulating. Up to 95% black, calculated on weight of rubber and black, can be obtained. There is an alternative method using a rubber solution in place of latex ; a dustless black is thus produced which contains no dispersing agent or other impurities not required in the final product.[124]

An important paper deals with the fundamental characteristics of channel and H.A.E. blacks indicating the methods used to evaluate performance factors. Although M.P.C. black has a smaller particle size and a narrower particle size distribution, it is nevertheless less reinforcing when compared with H.A.F.

It is shown that the amount of 'bound' rubber is a function of the surface area, so that theoretically the MPC should be superior to HAF. It is therefore suggested that the actual superiority of HAF is due to the smaller amount of chemisorbed surface oxygen, thus giving a better cure.

This is borne out by the improvement in the reinforcement properties of channel blacks after this oxygen has been removing by calcining; furnace blacks are affected much less. It is therefore suggested that by suitable compounding and processing the properties of channels can be improved and their relative deficiency overcome.[125] The properties of channel and furnace types are also compared by D. Parkinson who outlines their respective manufacturing processes. He concludes that, although the fine furnace types may be difficult to process owing to a high rate of scorch, they impart properties to vulcanized rubber at least equal to those produced by channel blacks.[126]

The production of black by grinding carbonaceous matter has been studied. The smallest particle size achieved was 100 mμ., but the iodine adsorption tests lead the authors to conclude that this is the diameter of undispersable clusters, and that the ultimate particles were 10 mμ. to 20 mμ.[127]

The emergence of a new white compounding ingredient with reinforcing properties similar to EPC black is an event of considerable importance. Hi-Sil, a hydrated silicon dioxide, is now available on the American market and its properties have been described. The particle size is the same as EPC black (0·025 μ.) and it is claimed to impart high tensile strength, good abrasion resistance, and exceptional tear resistance to both natural and synthetic rubber compounds. The properties of natural rubber vulcanizates containing various loadings of Hi-Sil have been compared with those of similar vulcanizates containing loadings of the black. All the properties of the Hi-Sil vulcanizates were claimed to be superior to those of the black vulcanizates. It is stated to be an extremely adsorptive material and therefore, it is necessary to use more than the normal amount of accelerator and more than the normal amount of fatty acid may be required.[128] The value of a compounding ingredient of this description is that it makes possible the production of light and coloured articles with physical characteristics comparable with those obtained by using carbon blacks.

Other light-coloured reinforcing fillers have also claimed attention during the year under review, mainly originating in the sterling area. Cryptocrystalline clays, mixed with one or more primary or secondary aliphatic or acrylic amines are compounded to give vulcanizates which have properties that are often equal or superior to those containing black. The extreme structural fineness of the clays used and the peculiar nature of the surface action between clay particles and the rubber macromolecules is suggested to explain these properties.[129,130,131]

Another product, which consists of specially treated aluminosilicates, is also claimed to compare favourably with carbon blacks. Tensile strength higher than that given by channel black is attained and heat build-up is much lower, but tear resistance is not as good as with carbon blacks. Results and charts are given reporting experimental work on various accelerator combinations.[132]

There has been evidence of a revival of interest in the possibilities of lignin as a reinforcing agent in rubber. T. R. Dawson has given a review of its chief chemlcal and physical properties and outlined the various proposals for its use. Figures are also given showing that the supply

of available lignin is almost unlimited. Its proposed use is traced from 1929, but it is only in the last few years that attention has been concentrated on its possibilities as a reinforcing agent. The properties vary according to the raw materials and processes used and this also makes it impossible to determine either the empirical formula or the molecular weight. It is reported that abrasion, tearing, tensile strength and hardness properties compare with those of channel black. All these results depend on the latex mixture being used but it is stated that the mixing of lignin emulsions into dry rubber may also lead to equally interesting properties.[133]

The reinforcing effects of lignin in GR-S has also been observed by American chemists and additional experimental work in Canada is reported.[134,135]

The use of GR-S in tyres has necessitated changes in methods of reclaiming tyre scrap and H. A. Winkelmann has made comparisons between commercial whole-tyre alkali and neutral process reclaim that are of interest to the rubber technologist. Water absorption, resilience, compression set, low-temperature brittleness and flexing tests were made in addition to the usual physical tests before and after oven ageing. In a natural rubber test compound alkali reclaims give high water-absorption, higher resilience, greater resistance to flex cracking and lower torsional hysteresis, whereas neutral reclaims give lower compression set and better low-temperature characteristics.[136]

An interesting patent relating to the manufacture of factice claims to improve the product by the addition of iodine to the reactants. This accelerates the reaction, the factice contains less free sulphur and the properties of a rubber vulcanizate containing it are better than those of a rubber made with an ordinary factice. Free sulphur was reduced to 1·9% compared with 4·1% for a similar mix without iodine.[137]

A further patent in the same field mentions the use of shark oil instead of rape oil, and this is claimed to increase the tensile strength of a rubber mix made with it.[138]

Analysis

The development of synthetic polymers and the improvement of carbon blacks has introduced analytical problems and has resulted in some noteworthy advances in analytical techniques. Standard procedures for the determination of carbon black in rubber have usually involved either the chemical degrading of the organic matter by nitric acid or the dissolution of the rubber in a solvent. These procedures are time-consuming and frequently inaccurate. A more rapid and accurate method has been reported by Bauminger and Poulton in which volatile matter is driven off by distillation in an atmosphere of nitrogen, and the carbon in the residue determined by combustion and absorption of the carbon dioxide. An interesting feature of the method lies in the additional possibility of estimating volatile matter associated with the black and so permitting some idea to be formed of the type of black present.[139]

Another important contribution giving speed and accuracy in the analysis of the organic material present has appeared. The estimation of styrene has previously been a rather cumbersome operation, but a

method has been reported which appears to be more straightforward and accurate. The polymer is depolymerized by heat in the presence of steam, the distillate nitrated and its colour examined. The whole procedure is conducted under carefully controlled conditions and is stated to be particularly adapted for the analysis of polystyrene, co-polymers of butadiene and styrene, and of 'popcorn.'[140]

Vulcanized rubber

A predominant place has been taken in the year's literature on vulcanized rubber by studies on the application of mathematical theory to the examination of structure and dynamic behaviour. A presentation of the network theory has been made by H. M. James and E. Guth[141] who discuss the approximations implicit in the use of the Gaussian network model for soft vulcanized rubber and show that the form of the stress–strain curve can be derived from this model simply and without special assumptions about the form or behaviour of the network. The common assumption that the network junctions are fixed is regarded as unrealistic and the authors conclude by giving a simple calculation of network entropy. A paper on the statistical theory of rubber-like elasticity[142] has given a method of calculation based on the principles of statistical mechanics making no use of the Gaussian law of distribution, and the relationship between the Gough–Joule coefficients and the moduli of vulcanized natural and synthetic rubber has been investigated by F. S. Conant *inter alia.*[143]

In a comprehensive treatment of the mechanical properties of rubber, A. H. Willis[144] has enumerated the many problems still needing elucidation. Although dynamic resilience is dependent on temperature, its dependence (and that of dynamic modulus) on frequency are not so certain. Dynamic fatigue under compressive stress depends on the temperature and a 'mechanical component of fatigue.' Incipient crystallization in stretched vulcanized rubber has been examined and an experimental determination of the elongation at which crystallization commences has been attempted through the measurement of density changes by a hydrostatic method.[145] An examination of the variation of specific heat in stretched rubber has given some support to Vogt's theory, valid for non-crystallized rubber, that the specific heat is independent of elongation,[146] and mathematical studies have been made of relaxation phenomena[147] and a constant-stress method for elongation.[148] An instrument has also been described for determining relaxation and recovery.[149]

The significance of crystallization in rubber at low temperatures has been examined,[150] correlation with X-ray data showing that crystallization is responsible for stiffening. It is stated that the rate of change of stiffness increases rapidly with increase in applied stress and there is no optimum temperature as there is with unstressed rubber. Progressive stiffening at low temperatures has also been studied by measuring the relative torsional modulus of test strips of natural and synthetic rubber compounds over a period of 30 days at $-60°$ to $-20°$ C.[151]

A theory of non-linear viscous elasticity has been propounded by H. Burte and G. Halsey[152] who recognize two extreme types of visco-elastic behaviour: (i) elongation of a material accompanied by an increase

in potential energy because the molecules are strained uniformly into new positions and (ii) flow, in which a section of the molecular segment originally with a configuration A assumes an entirely new configuration B and thereby becomes unable to move again. Except for a small elastic deformation of both structures, the elongation is proportional to the fragment of the section which is in the B configuration. The two components are assumed to be in solution with one another and the rates of transformation are then proportional to the relative abundance of the transformed species. In a further study of non-linear viscous elasticity, G. D. Halsey[153] discards the spring-dashpot model in favour of models based on the rupture of secondary bonds. The presence of bonds in parallel, on which the stress concentrates owing to breakage, allows thixotropic humps and rupture to be explained.

R. S. Rivlin has continued his series of mathematical studies, mentioned in last year's report, on large elastic deformations of isotropic materials. In previous papers a theory was developed on the basis of a law for the elastic behaviour of rubber, which arises from the kinetic theory of high elasticity and is, from the mathematical point of view, the simplest law that could be employed. In the present paper[154] it is stated that the equations of motion, boundary conditions and stress–strain relations for highly elastic material can be expressed in terms of the stored energy function, which may be defined for a particular material in terms of the invariants of strain. In dealing with the problem of flexure, these principles are used by the same worker to calculate the surface tractions which must be applied in order to maintain the state of flexure.[155]

An evaluation of flex-life and heat build-up properties has been made[156] on the basis of the establishment of linear correlations between those properties and the state of cure measured by the dynamic compression of the vulcanizate. Some critical comments on resilience testing have been offered in a German paper,[157] the points considered including elastic modulus effects, resilience test evaluation and dependence on impact energy; the relation between elastic properties and cross-linking has been examined by P. J. Flory and N. Rabjohn,[158] who have compared the elastic properties of various rubbers vulcanized to different degrees of cross-linking through the use of diazodicarboxylates with those of the usual sulphur-accelerator vulcanizates. An extension of these investigations has included a determination of the tensile strengths of rubbers quantitatively cross-linked with decamethylene dimethyl azodicarboxylate and a theoretical discussion has been given on the relationship between tensile strength and network structure.[159] Tensile strength and elongation at break have been determined over a temperature range of from $-10°$ c. to $120°$ c. for vulcanizates based on natural and synthetic rubbers.[160] The natural rubber vulcanizates are shown to have a much higher heat resistance than the synthetic rubbers, with much better preservation of tensile properties at higher temperatures. Natural rubber also retains its elongation almost unchanged at elevated temperatures whereas synthetic rubbers show a considerable drop.

A high speed stress–strain machine has been developed capable of recording the stress–strain curve of rubbers at rates up to 27% per millisec. and a description has been given[162] of an angular horizontal

tensile testing apparatus intended for testing materials of small section. The speed control is variable through eight steps from 0·1 to 20 in./min. and the tensile load applied is balanced by the deviation of the pendulum from the vertical position. A comparison of tensile data from ring and dumb-bell specimens has been made by J. R. Scott[163] who discusses the calculation of true tensile strength from ring data, and an examination has been made[164] of the influence of the material forming the mould surface on the tensile and ageing properties of rubber vulcanized in moulds. The best finish to the rubber surface was given by stainless steel plates.

A systematic study has been made[165] of the stress–strain curves for a pure gum natural rubber in order to examine the hysteresis phenomena in rubber undergoing cyclic strains of very low frequency. The successive cycles of elongation and recovery have been recorded with a dynamometer between two limiting elongations, the smaller having a value between 0 and maximum elongation. The tests, carried out sometimes up to 1000 cycles, appear to confirm that plastic flow and internal friction have only a small influence, so it can be assumed that the hysteresis effect is due to crystallization by elongation. In a further paper on hysteresis[166] the same author points out that according to the temperature, rate and magnitude of deformation several phenomena may cause hysteresis of rubber under mechanical stresses varying with time. For rapid deformations of small amplitude such as exist in a state of vibration the observed loss of energy results mainly from internal friction. A hysteresis test has been developed by M. Mooney and S. Black[167] which measures directly the energy loss per cycle of elongation, and a description has been published[168] of a Roelig type of testing machine in which the test-piece, under compression loading, is mechanically oscillated by means of a continuously adjustable eccentric weight rotated by a variable speed motor.

The extensive interest shown during the year in the ageing of rubber has been marked by the publication of a 'Symposium on Ageing of Rubbers' by the American Society for Testing Materials,[169] containing papers on the mode of attack of oxygen on rubber, oxygen-absorption methods in the study of ageing, physical aspects of ageing, effects of light and ozone on rubber and the effect of temperature on air ageing. In dealing with the physical aspects of ageing, M. C. Throdahl[170] has recapitulated the evidence suggesting that ageing or degradation is similar in nature to polymerization, the reactions involved being chain mechanisms, the physical changes of which are the net sum of several simultaneous processes; (i) cross-linking, cyclization, and continued polymerization which harden and stiffen the rubbers and (ii) scission, which produces tackiness and results in loss of tensile strength. The three methods commonly employed for oxygen-absorption studies (i.e. gravimetric, manometric and volumetric) have been discussed by J. R. Shelton[171] who comments on the possibility of such methods being used as a test for predicting the relative resistance to ageing in service; M. J. Schoch[172] has contributed a report on the effect of the temperature of exposure in an air ageing test on the rate of deterioration of the properties of typical vulcanizates. The results show that over the temperature range of 70° to 125° C. the rate of deterioration is dependent on temperature

and the temperature coefficient of ageing varies between 1·82 and 2·87/10° c. depending on the composition of the material and the property being measured. The symposium also includes a paper by J. T. Blake[173] on the action of light and ozone on rubber and the variety of ways in which it is manifested.

In an earlier paper on the ageing of elastomers, M. C. Throdahl[174] has commented on the shortcomings of the conventional oven and bomb tests in estimating ageing characteristics, and has advocated a method based on creep and stress relaxation measurements which has proved satisfactory in evaluating antioxidants, the results being independent of the accelerator used and of the period of vulcanization; W. E. Phillips[175] has described a new accelerated static weathering test in which samples are mounted over a metal reflector for the purpose of exposing both sides of the sample simultaneously to the action of sunlight. This author also points out the value of physical tests such as stress–strain in evaluating the rate of ageing. The causes of ageing in vulcanized rubber have been discussed by a Japanese worker[176] in connexion with the oxidation of combined sulphur. Part of the combined sulphur is evolved, during ageing by heating, in the form of hydrogen sulphide; hence, oxidation takes place and the author explains both the fact that vulcanizates containing approximately 7% combined sulphur are most vulnerable to ageing as well as the contradiction between the antioxidizing phenomenon and durability.

For some time past, techniques have been developed for the use of sonic and ultrasonic wave measurements as a means of relating the mechanical properties of polymers to molecular characteristics, and methods are now being applied in a systematic way to secure new information on molecular constellations, rigidities, and slippage.[177] The velocity and attenuation of supersonic waves in natural and synthetic rubbers have been studied by D. G. Ivey, B. A. Mrowca and E. Guth[178] following on the earlier work of A. W. Nolle and S. C. Mowry.[179] Bulk stocks of *Hevea*, GR-S and Butyl have been studied at 50 kc. to 10 mc. and from − 50° to 60° c. and it has been found that for all stocks tested the velocity increases with frequency or decreases with temperature, levelling off at low temperatures. These results are in qualitative agreement with data obtained by the strip method at lower frequencies, but for bulk waves the real and imaginary parts of two elastic constants (bulk and shear moduli) determine sound velocity and attenuation. The measurements extend the frequency range studied previously by the strip method and thus give a qualitative knowledge of the relaxation spectrum over a wide range. Elastic losses of natural rubber and butadiene–styrene copolymers at ultrasonic frequencies have been examined by H. S. Sack and R. W. Aldrich[180] over a frequency range of 0·5 to 6 mc. In general, the absorption per wavelength increases with increasing frequency, but the increase is less rapid at higher frequencies. Loaded samples show a higher absorption, and, as in the low frequency range, the losses in the copolymers increase with increasing styrene content and with decreasing temperature.

The electrical properties of vulcanized rubber have been given a fairly comprehensive review by J. Shimizu, *inter alia*,[181] who discusses the

influence of various types of rubbers and compounding ingredients on the vulcanized product from the point of view of such properties as breakdown voltage, specific resistivity, dielectric constant and conductance/capacity; in a fundamental study on dielectric properties, S. Kambara[182] has investigated the relation between the basic dipole moment and the vulcanization of rubber–sulphur mixtures. With increasing vulcanization it has been found that the dipole moment at first increases and then decreases and this is attributed to depolymerization by over-vulcanization. Experiments on the dielectric loss in swollen rubbers (natural and neoprene) have been described[183] and it has been shown that the dielectric loss–tangent curves of swollen rubbers as a function of the temperature have one maximum if the swelling agent is non-polar, but two maxima if it is polar. Different relaxation mechanisms are suggested by the experimental results and it is thought these are a specific effect of the chain structure of the rubbers.

Increasing attention has been given to the application of high-frequency heating in various branches of the rubber industry[184,185,186,187,188] and both induction and dielectric methods have been outlined by L. E. Pearson.[189] Induction heating depends in principle on the production in the work of eddy currents by a coil of wire carrying a current of frequency varying from 50 to 500,000 cycles; the eddy currents are dissipated as heat throughout the material, which must be a good conductor of electricity. High-frequency dielectric heating has been discussed by L. Mullins and D. J. Hine[190] who emphasize the necessity of homogeneity in the stock to be treated and point out the difficulty of applying dielectric techniques to vulcanizing under pressure in that this calls for moulds which have to be both of insulating material and at the same time of sufficient strength. The high-frequency heating of bulk objects before vulcanization has been described mainly[191] in connexion with foam latex mattresses and a detailed account has been given of the application of dielectric heating to radio coagulation of latex, drying of products with latex base, heating before moulding and in the mould, the production of porous rubber and the reclaiming of rubber. The use of infra-red heating has been discussed[193] mainly in relation to heating, drying, vulcanizing, stoving and glossing; further possibilities in the application of infra-red rays in the rubber industry have been reviewed by K. H. Budig[194] who gives a description of the Philip's apparatus and installations for lacquer and fabric drying and the drying of powdered fillers.

References

1 Cook, T. G., *India Rubb. World*, 1948, **119**, 227
2 Vila, G. R., ibid., 1949, **120**, 592
3 de Haan, I. and van Aggelen-Bot, G. M., *Rubb. Age, N.Y.*, 1949, **64**, 589
4 Altman, R. F. A., *India Rubb. J.*, 1949, **117**, 502
5 Johnson, J. R. and Gerzon, K., *India Rubb. World*, 1949, **120**, 712
6 van Gils, G. E., *Rubb. Age Synth.*, 1949, **30**, 16
7 de Haan-Homans, L. N. S., *India Rubb. J.*, 1949, **116**, 331
8 B.P. 612,443
9 B.P. 621,998
10 Lawrence, A. S. C., *Chem. & Ind.*, 1949, 173
11 Gardiner, K. W., *Rubb. Age, N.Y.*, 1948, **64**, 66
12 Thirion, P., *Rev. gén. Caoutch.*, 1949, **26**, 176

[13] Belmas, R., ibid., 341, 505
[14] Dawson, H. G., *India Rubb. World*, 1948, **119**, 225
[15] Stevens, W. H., *Rubb. Develop.*, 1949, **2**, No. 2, 14
[16] Cosset, R., *Rev. gén. Caoutch.*, 1948, **25**, 120 D
[17] Sibiriakoff, I., ibid., 478; 1949, **26**, 21
[18] Lumsdale, R. A., *Bergcultures*, 1948, **17**, 142
[19] van Gils, G. E., ibid., 1949, **18**, 51, 53
[20] Silvernail, L. H., *Chem. Abs.*, 1949, **43**, 6410
[21] Blow, C. M., *India Rubb. J.*, 1949, **116**, 228
[22] Canad. P. 457, 436
[23] Hooreman, M. and Lepetit, F., *Rev. gén. Caoutch.*, 1948, **25**, 90
[24] Lepetit, F., ibid., 1949, **26**, 167
[25] B.P. 614,434
[26] U.S. Rubber Co., *Rubb. Age Synth.*, 1949, **30**, 296
[27] McKay, R. F., *Rubb. Develop.*, 1949, **2**, No. 1, 1
[28] Crisp, P. P., ibid., 1948, **1**, No. 6, 10
[29] Conant, F. S. and Wohler, L. A., *Rubb. Age, N.Y.*, 1949, **65**, 57
[30] B.P. 622,159
[31] B.P. 618,604
[32] U.S.P. 2,441,235
[33] U.S.P. 2,463,289
[34] U.S.P. 2,475,191
[35] B.P. 619,619
[36] U.S.P. 2,466,027
[37] B.P. 611,164
[38] B.P. 611,165
[39] U.S.P. 2,472,055
[40] U.S.P. 2,472,054
[41] Bugeon, M., *Rubb. Develop.*, 1948, **1**, No. 6, 23
[42] B.P. 608,561
[43] British Rubber Producers' Assoc., *Rubb. Develop.*, 1949, **2**, No. 2, 13
[44] Stevens, W. H., ibid., 1948, **1**, No. 6, 4
[45] Vernon, W. H. J., *Plastics (Lond.)*, 1949, **13**, 116
[46] London Advisory Committee for Rubber Research (Ceylon and Malaya), Annual Report, 1948
[47] Verghese, G. T., *Trans. Instn. Rubb. Ind.*, 1948, **24**, 138
[48] Idem, ibid., 274
[49] Idem, ibid., 280
[50] Stevens, H. P., *India Rubb. J.*, 1948, **117**, 503
[51] Dawson, T. R., *Rubb. Develop.*, 1948, **1**, No. 6, 1
[52] B.P. 615,866
[53] U.S.P. 2,446,075
[54] Neal, A. M. and Vincent, J. R., *Rubb. Age, N.Y.*, 1949, **64**, 728
[55] Cole, J. O., ibid., 728
[56] Bateman, L. and Gee, G., *Proc. roy. Soc.*, 1948[A], **195**, 376
[57] Idem, ibid., 391
[58] Bolland, J. L., *Quart. Rev. chem. Soc.*, 1949, **3**, 1
[59] Bolland, J. L. and Ten Have, P., *Trans. Faraday Soc.*, 1949, **45**, 93
[60] Hencky, H., *Research*, 1949, **2**, 437
[61] Rössler, F., *Z. angew. Phys.*, 1948, **1**, No. 2, 50; *Science Abs.*, 1949, **52A**, 151
[62] Furukawa, J. and Tomihisa, K., *J. Soc. Rubb. Ind. Japan*, 1948, **21**, 17, 19, 46; *Chem. Abs.*, 1949, **43**, 2010
[63] Kambara, S., *J. Soc. Rubb. Ind. Japan*, 1942, **15**, 927; *Chem. Abs.*, 1949, **43**, 5221
[64] Steiner, L. A., *Chem. Age*, 1949, **60**, 638
[65] de Bruyne, N. A., *Rubb. Age Synth.*, 1949, **30**, 180
[66] Mann, J., *J. Rubb. Res.*, 1949, **18**, 79, 89
[67] Sutherland, G. B. B. M., *Bull. Brit. sci. Instr. Res. Ass.*, 1949, **4**, 246
[68] Idem, *Instrum. Pract.*, 1949, **3**, 190
[69] Idem, ibid., 232
[70] Cropper, F. R. and Hamer, A., *J. Text. Inst., Manchr*, 1949, **40**, 345A
[71] Research Association of British Rubber Manufacturers, *India Rubb. J.*, 1949, **116**, 485
[72] Anderson, J. A. and Seyfried, W. D., *Analyt. Chem.*, 1948, **20**, 998

[73] King, G. W., Hainer, R. M. and McMahon, H. O., *J. appl. Phys.*, 1948, **20**, 559
[74] Gee, G., *India Rubb. J.*, 1949, **116**, 771
[75] Hauser, E. A., *Rubb. Age, N.Y.*, 1949, **64**, 499
[76] Melville, H. W., *Chem. & Ind.*, 1949, No. 6, 83
[77] Miller, A. R., *Endeavour*, 1949, **8**, 140
[78] Idem, *Nature*, 1949, **163**, 838
[79] Nee, W., *Corrosion Rep.*, 1948, **4**, 599
[80] Martin, J. B., *Canad. Chem.*, 1949, **33**, 208
[81] Kambara, S. and Muramatsu, Y., *Chem. Abs.*, 1949, **43**, 1594
[82] Dawson, T. R., 'Elastomers and Plastomers,' Vol. II, 1949, 402
[83] B.P. 348,303; 523,734
[84] Stern, H. J., *Rubber Age Synth.*, 1948, **29**, 360
[85] Firestone, H. S., *Rubb. Age, N.Y.*, 1949, **65**, 196
[86] O'Neil, W., ibid., 199
[87] Anon., *Rubb. Age Synth.*, 1949, **30**, 171
[88] Dinsmore, R. P., *Tires*, 1949, **30**, No. 6, 28
[89] Fielding, J. H., *Ind. Eng. Chem.*, 1949, **41**, 1560
[90] Laundrie, R. W. and McCann, R. F., ibid., 1568
[91] Drogin, I., Bishop, R. and Wiseman, P., *Rubb. Age, N.Y.*, 1948, **64**, 309
[92] Nellen, A. H., Dunlap, W. B. and Glaser, C. J., *India Rubb. World*, 1949, **120**, 57
[93] Sheppard, D. M., *Rubber Age, N.Y.*, 1949, **65**, 78
[94] Steffen, H. C., *India Rubb. World*, 1949, **120**, 60
[95] Sjothun, I. J. and Cole, O. D., *Ind. Eng. Chem.*, 1949, **41**, 1564
[96] Stanger, E. L. and Radcliff, R. R., ibid., 1603
[97] Fryling, C. F., Landes, S. H., St. John, W. M. and Uraneck, C. A., ibid., 986
[98] Wall, F. T. and Swoboda, T. J., *J. Amer. chem. Soc.*, 1949, **71**, 919
[99] Mitchell, J. M., Spolsky, R. and Williams, H. L., *Ind. Eng. Chem.*, 1949, **41**,1592
[100] Hobson, R. W. and D'Ianni, J. D., *Rubb. Age, N.Y.*, 1949, **65**, 547
[101] Mast, W. C. and Fisher, C. H., *Ind. Eng. Chem.*, 1949, **41**, 703
[102] Meyer, A. W., ibid., 1570
[103] Flanagan, G. W., *Rubb. Age, N.Y.*, 1949, **65**, 193
[104] Young, D. W., Buckley, D. J. and Newberg, R. G., *Ind. Eng. Chem.*, 1949, **41**, 401
[105] Bascom, R. C., *Mod. Plastics*, 1949, **27**, 84
[106] Hatsch, R. E., *Rubber Age, N.Y.*, 1949, **65**, 204
[107] Haworth, J. P., *Ind. Eng. Chem.*, 1948, **40**, 2314
[108] True, O. S., *Chem. Engng.*, 1949, **56**, 263
[109] Anon., *Plastics News Letter*, 1949, **9**, No. 23, 4
[110] Forman, D. B., Mayo, L. R. and Radcliff, R. R., *India Rubb. World*, 1949, **120**, 715
[111] Mayo, L. R., *Rubb. Age, N.Y.*, 1949, **65**, 234
[112] Mochel, W. E., Salisbury, L. F., Barney, A. L., Coffman, D. D. and Mighton, C. J., *Ind. Eng. Chem.*, 1948, **40**, 2285
[113] Stacey, M., *Industr. Chem. chem. Mfr.*, 1949, **25**, 112
[114] Chipman, A. D., Schmidt, H. F. and Konkle, G. M., *Rubb. Age, N.Y.*, 1949, **65**, 545
[115] Chapman, F., *J. Oil Col. Chem. Ass.*, 1948, **31**, 203
[116] *Mod. Plastics*, 1949, **26**, No. 10, 174
[117] U.S.P. 2,482,888
[118] Anon., *Chem. Engng. News*, 1949, **27**, 2028
[119] Anon., *Plastics News Letter*, 1949, **9**, No. 23, 4
[120] Hardy, D. V. N., *Paint Technol.*, 1949, **14**, 114
[121] Dawnay, C. P., *India Rubb. J.*, 1949, **117**, 214
[122] B.P. 621,031
[123] B.P. 623,600
[124] B.P. 625,872
[125] Dannenburg, E. M. and Collyer, H. J., *Ind. Eng. Chem.*, 1949, **41**, 1607
[126] Parkinson, D., *Trans. Inst. Rubb. Ind.*, 1949, **24**, 267
[127] Bremmer, J. G. M. and Colpitts, J. H., ibid., 1948, **24**, 35
[128] Allen, E. M., Cage, F. W. and Wolf, R. F., *Rubber Age, N.Y.*, 1949, **65**, 297
[129] F.P. 928,711
[130] *Rev. gén. Caoutch.*, 1949, **26**, 143
[131] B.P. 616,069
[132] *Franterre Tech. Bull., Trimestriel*, 1949, No. 5, 37
[133] Dawson, T. R., *Trans. Instn. Rubb. Ind.*, 1949, **24**, 227
[134] Raff, R. A. V., *Canad. Chem.*, 1949, **33**, No. 1, 35

[135] Anon., *India Rubb. J.*, 1949, **116**, 221
[136] Winkelman, H. A., *Rubb. Age, N.Y.*, 1949, **65**, 57
[137] B.P. 615,395
[138] B.P. 616,215
[139] Bauminger, B. B. and Poulton, F. C. J., *Analyst*, 1949, **74**, 351
[140] Crippen, R. C. and Bonilla, C. F., *Analyt. Chem.*, 1949, **21**, 927
[141] James, H. M. and Guth, E., *J. Polymer Sci.*, 1949, **4**, 153
[142] Sakai, T. and Isihara, A., *J. Colloid Sci.*, 1949, **4**, 71
[143] Conant, F. S., Hall, G. L. and Thurman, G. R., *Rubb. Age, N.Y.*, 1949, **64**, 484
[144] Willis, A. H., *Rubb. Age Synth.*, 1949, **30**, 19, 22, 24, 58, 62, 94, 98, 100
[145] Fox, T. G., Flory, P. J. and Marshall, R. E., *J. chem. Phys.*, 1949, **17**, 704
[146] Mayor, A. R. and Boissonnas, C. G., *J. Text Inst., Manchr*, 1949, **40**, 78**A**
[147] Schay, G., *Chim. Belges*, 1948, **57**, 170; *Chem. Abs.*, 1949, **43**, 2459
[148] Dahlquist, C. A., Hendricks, J. O. and Taylor, N. W., *India Rubb. World* 1949, **120**, 91
[149] Phillips, W. E. and Labbe, B. G., ibid., 1948, **119**, 224
[150] Beatty, J. R. and Davies, J. M., ibid., 1949, **119**, 614
[151] Gehman, S. D., Jones, P. J., Wilkinson, C. S. and Woodford, D. E., ibid., **120**, 716
[152] Burte, H. and Halsey, G., *Text. Res. J.*, 1947, **17**, 465; *Chem. Abs.*, 1948, **42**, 8479
[153] Halsey, G., *Rubb. Age, N.Y.*, 1949, **64**, 483
[154] Rivlin, R. S., *Philos. Trans.*, 1948, **241(A)**, 379
[155] Idem, *Proc. roy Soc.*, 1949[A], **195**, 463
[156] Storey, E. B., *India Rubb. World*, 1949, **120**, 213
[157] Späth, W., *Gummi u. Asbest*, 1949, **2**, 57, 180
[158] Flory, P. J. and Rabjohn, N., *J. Polymer Sci.*, 1949, **4**, 225
[159] Flory, P. J., Rabjohn, N. and Shaffer, M. C., *Rubber Age, N.Y.*, 1949, **64**, 483
[160] Boonstra, B., *India Rubber J.*, 1949, **117**, 460, 463
[161] Villars, D. S., *Rubb. Age, N.Y.*, 1949, **65**, 544
[162] Buehler, A. I., *A.S.T.M. Bull.*, 1948, No. 155, 2
[163] Scott, J. R., *J. Rubb. Res.*, 1949, **18**, 30
[164] R.A.B.R.M., ibid., 1948, **17**, 203
[165] Clouaire, J., *Rev. gén. Caoutch.*, 1949, **26**, 85
[166] Idem, ibid., 626
[167] Mooney, M. and Black, S., *Rubb. Age, N.Y.*, 1949, **65**, 193
[168] Wilkinson, C. S. and Gehman, S. D., ibid., 57
[169] American Society for Testing Materials, Symposium on Ageing of Rubbers, Special Technical Publication, No. 89
[170] Ibid., 35
[171] Ibid., 12
[172] Ibid., 59
[173] Ibid., 48
[174] Throdahl, M. C., *Ind. Eng. Chem.*, 1948, **40**, 2180
[175] Phillips, W. E., *Rubb. Age, N.Y.*, 1949, **65**, 57
[176] Okita, T., *J. Soc. Rubb. Ind. Japan*, 1942, **15**, 96; *Chem. Abs.*, 1949, **43**, 2023
[177] Smith, T. L., Ferry, I. D. and Schremp, F. W., *J. appl. Phys.*, 1949, **20**, 144
[178] Ivey, D. G., Mrowca, B. A. and Guth, E., *Rubb. Age, N.Y.*, 1949, **64**, 482
[179] Nolle, A. W. and Mowry, S. C., *J. acoust. Soc. Amer.*, 1948, **20**, 432
[180] Sack, H. S. and Aldrich, R. W., *Rubb. Age, N.Y.*, 1949, **64**, 483
[181] Schimizu, K., *J. Soc. Rubb. Ind. Japan*, 1948, **21**, 1
[182] Kambara, S., ibid., 1942, **15**, 743; *Chem. Abs.*, 1949, **43**, 3223
[183] Schallamach, A. and Thirion, P., *Trans. Faraday Soc.*, 1949, **45**, 605
[184] B.P. 623,736
[185] B.I.P. Tools, Ltd., *Plastics (Lond.)*, 1949, **13**, 289
[186] B.P. 609,310
[187] Gams, T. C., *Electronics*, 1948, **21**, No. 9, 83
[188] La Rose, W. T., *Plastics World*, 1949, **7**, No. 1, 1
[189] Pearson, L. E., *Rubb. Age Synth.*, 1949, **30**, 222, 224
[190] Mullins, L. and Hine, D. J., *J. Rubb. Res.*, 1949, **18**, 99
[191] Mielke, E. S., *India Rubb. World*, 1949, **119**, 485
[192] Le Bihan, Y. and Spanjaard, L. P., *Rev. gén. Caoutch.*, 1949, **26**, 15
[193] Anon., *India Rubb. J.*, 1949, **116**, 562
[194] Budig, K. H., *Kautschuk u. Gummi*, 1949, **2**, 213

PULP AND PAPER

By E. L. HILL, B.Sc., A.R.C.S.
Ministry of Supply

WORLD wood pulp problems were considered at a conference held in Montreal in the spring, under the auspices of the Food and Agricultural Organization of the United Nations.[1] For the period 1948–55 dealt with by the conference it was predicted that production and requirements would be in fairly close balance; no major pulp surplus or shortage was therefore likely to develop. Despite idle capacity, estimated at 4·3 million tons in Europe and at 1 million tons in the rest of the world (mainly in Japan), world wood pulp production in 1948 was the highest on record. The predominant position of the North American continent, both as a producer, with 68%, and as a consumer, with 70%, of the world total, has become very marked since the war. In Western Europe it was foreseen that a problem will arise in bringing all existing pulp capacity into operation: the European forests will be incapable of providing the additional quantity of pulp-wood required, and it is not clear from what other sources supplies can be obtained. With a view to stimulating the development of production in new areas, the conference recommended the setting up of technical Committees to study the pulping of (*a*) tropical woods and (*b*) straw and other agricultural wastes. These bodies have now started work under the aegis of F.A.O.

For the British paper industry, the year has seen the progressive relaxation of controls, culminating in the announcement of the end of Paper Control buying of wood pulp and esparto, which now revert to private purchase. Increased production of many types of paper has been permitted but the output of newsprint, although rising, has remained substantially below the pre-war figure. Board production, on the other hand, has expanded notably and is now considerably above the pre-war level. Paper prices have moved steadily downwards.

Paper-making raw materials were in freer supply and wood pulp prices showed a downward trend but, late in the year, after the devaluation of sterling, Scandinavian pulp prices hardened.

Raw materials

Wood.—E. J. Schreiner[2] has given an account of the work carried out in the U.S.A. on the breeding of hybrid poplars for pulp-wood. On the basis of experience in Maine it is predicted that, with good forestry methods, plantations should yield 10 cords per acre of thinnings at 8–10 years and 30 cords per acre of pulp-wood at 15 years after planting. Hitherto hybrid poplars have suffered from two serious disadvantages: susceptibility to disease and the need for special care in planting and cultivation. Research is therefore now being directed to the breeding of disease-resistant hybrids. The morphological and chemical characteristics of European poplar, in relation to its utilization for the manufacture of paper and dissolving pulps, have been discussed in detail by G. Jayme.[3]

The desirability of achieving more complete utilization of forest resources by the integration of lumber and pulp mills has given rise to several investigations. Thus J. S. Martin[4] has assessed the value, for kraft pulping, of logging and saw mill wastes of old-growth Douglas fir and of certain associated species, viz. mountain hemlock (*Tsuga mertensiana*), noble fir (*Abies procera*) and lodgepole pine (*Pinus contorta* var. *latifolia*). The Douglas fir included not only timber which, although sound, was unfit for lumber, but also wood which, in varying degrees, had been rotted by *Fomes pini* ('white pocket'). The effect of this organism on the kraft pulping properties of the wood was surprisingly slight; the yield from badly rotted wood was only 2% below that from sound wood. The bursting strength was, however, reduced when decaying wood was cooked but, since the minor species were found to give pulps with high bursting strength, it was possible, by the use of a mixture of decaying wood and the associated species, to produce pulp equal in quality to that produced from sound Douglas fir.

The influence of age and growth conditions on the sulphate-pulping properties of Douglas fir has been studied by R. N. Hammond and F. S. Billington.[5] The wood used, which varied in age between 30 and 350 years, represented sound old growth, mature second growth, pre-logged timber and thinnings. In general the younger wood gave slightly higher yields of pulp of higher bursting strength but lower tearing strength.

The study of the pulping properties of North American hardwoods continues under the stimulus of the increasing shortage of the preferred species and the knowledge that the felling of the hardwoods with the softwoods is better forestry practice. The grinding characteristics of seven hardwood species have been examined by A. Hyttinen and E. R. Schafer,[6] who found them all to yield pulps lower in strength than those prepared under comparable conditions from the commonly used softwoods. By blending with stronger pulps, acceptable papers could be made from them—with the exception of the pulps from two of the woods which were dark and would find limited application in an unbleached state. R. S. Aries[7] states that mixtures of hardwoods consisting of about 70% white and red oak, together with beech, birch, maple and hickory, can be pulped satisfactorily by either the sulphate or the neutral sulphite semi-chemical process.

The declining availability of spruce in U.S.A. has led Z. A. Zasada and C. A. Richardson[8] to study the economics of thinning immature stands of black spruce and of utilizing thinnings with 3-in. minimum top diameter for the production of mechanical pulp. In practice 54% of the wood consisted of sticks 4 in. in diameter or larger. The logging cost per cord was considerably higher than when operating in a mature stand but the mechanical pulp produced did not differ in yield and quality from that manufactured from normal pulp wood.

The lengths of the fibres and vessel segments in 49 hardwoods indigenous to U.S.A. have been measured by S. I. Bergman[9] and the results analysed statistically. A guide to the identification of the fibres, chiefly wood pulps, encountered in Swedish paper manufacture has been prepared by B. Ivarsson.[10] Emphasis is placed on morphological characteristics and a number of useful photomicrographs is included.

Straw.—Experimental-scale trials have impressed S. I. Aronovsky and E. C. Lathrop[11] with the possibilities of pulping straw by treating it with steam and chemicals in a Hydrapulper at atmospheric pressure. Pulping time is greatly reduced. Strawboard pulp, for example, produced in one hour in the Hydrapulper, using 6% of lime and 1·5% of caustic soda, is similar in yield and properties to the pulp resulting from a five-hour pressure-cook at 140° c. using the same chemicals. Strong, easy-bleaching pulps can be made by treating straw for half an hour in the Hydrapulper with kraft cooking reagents. The liquor/straw ratio is higher in this process than in pressure digestion, and the concentration of organic matter in the black liquor is not high enough to make recovery practicable. The liquor may, however, be re-used, and, after the fourth cook, is approaching the level at which the recovery of reagent by the burning of the concentrated black liquor would be feasible. Another advantage claimed for the Hydrapulper is that nodes and seed grains are softened but not disintegrated, and are therefore capable of being almost completely eliminated by screening.

E. C. Lathrop and T. R. Naffziger[12,13] have made a structural insulating board from straw, which compares favourably with commercial insulating board produced from wood. Two different types of pulp are blended to form the board : a hydrated binder pulp produced by beating a normal, lime-cooked, strawboard pulp, and an unhydrated pulp containing long-fibred bundles made by chopping wheat straw to 1½in.-lengths, cooking in water at 40 lb./in.^{2} and refining in a Bauer mill. The authors have made a detailed investigation of the operating variables of the process.

Pulp production

Wood preparation.—In a short note on the chemical killing process, to which reference has been made in earlier Reports, D. C. McIntosh[14] has stated that experiments carried out in 1947 and 1948 have shown that the sap-peeling season can be extended and that peeling is made easier by killing the trees by chemical methods. The results also indicated that weight reduction, due to accelerated drying out, can be achieved with coniferous but not with broad-leaved species.

The problems involved in the measurement of pulp wood have been discussed by J. B. Jones,[15] who has given an account of a mill installation in which the volume of wood entering the stock pile is measured by a water-displacement method using two submerging cages holding approximately four cords each. Methods of volume measurement have also been considered by G. J. Brabender[16] who, for unsorted wood, was unable to find any relationship between stick diameter and solid volume per cord.

Recent developments in welded barking drums have been described by G. M. Dick.[17] W. G. Tamblyn[18] reports a considerable economy in fuel by the flash drying and burning of ground bark.

According to J. O. Murto and E. Kivimaa,[19] increasing the cutting angle of a four-bladed chipper leads to more rapid blunting of the blades, the production of thicker chips and an increase in power consumption, chip damage and the percentage of fines. A study of the effect of varying chip thickness between ½ and 7 mm. on the yield and quality of both

sulphate and sulphite pulps has led A. Backman[20] to conclude that there is a marked optimum at 3-mm. thickness.

Mechanical process.—Trends in the manufacture of groundwood in North America have been well reviewed by H. J. Perry.[21] The effect of operating variables on the performance of the Roberts grinder has been studied by R. S. Magruder,[22] who finds that by appropriately adjusting conditions it is capable of yielding a wide range of pulps, including a good grade of book stock. R. T. Wetmore and L. W. Dunphy[23] state that the poor ink penetration, particularly after ageing, of certain newsprints is related to a high resin content in the groundwood pulp from which it is manufactured. They recommend that, by using a higher grinder temperature and by using sulphuric acid in preference to alum in the paper mill, the resin content should be maintained below 0·3%. W. Brecht[24] has given details of the technique of producing strong pulp by increasing the content of long fibres and has also referred to a method for improving groundwood quality which depends on the separation of the pulp into coarse and short-fibred fractions.

Semi-chemical pulping processes.—The process adopted by the first Canadian mill to undertake the production of semi-chemical pulp has been described by J. C. W. Evans.[25] The chips are cooked for 4 hr. at 120° C. in spherical rotary digesters with alkaline sodium sulphite, made by the partial neutralization of soda ash with sulphur dioxide; they are then refined in Bauer mills. Yields are said to exceed 90%, and of 21 different wood species processed only one was considered unacceptable, namely western cedar, owing to the difficulty of pulping its bark.

It is standard practice in commercial semi-pulping by the neutral sulphite process to use an alkaline cooking-liquor in order to reduce digester corrosion and to improve pulp quality. The respective merits, in the semi-pulping of aspen, of the four most suitable alkaline buffering agents, viz. sodium bicarbonate, sodium carbonate, sodium hydroxide and sodium sulphide have been examined by E. L. Keller and J. N. McGovern.[26] Yields and pulp strengths were little affected by varying the buffer. Increasing the alkalinity of the buffer had an important effect in reducing cooking time but, on the other hand, the highest brightness values were obtained when only small quantities of buffer were used and the p_H of the spent liquor was almost neutral.

The high-yielding semi-chemical process finds its chief application in the production of pulp for corrugating board. J. N. McGovern, G. E. Mackin and G. H. Chidester[27] have explored the possibility of extending the field of application of the semi-chemical process to the production of stronger pulps capable of serving as a substitute for kraft in the manufacture of liner board. When jack pine and various hardwoods were cooked to give yields of between 70 and 80% the resulting pulps, although satisfactory in other respects, were deficient in folding- and tearing-strength when compared with southern pine kraft pulp. However, it was shown that by incorporating a proportion of southern kraft pulp in the furnish, the resulting liner board can be much improved. Further improvement in the finished fibre board can also be secured by replacing straw by aspen semi-chemical pulp in the manufacture of the

corrugating board. The use of semi-chemical pulp for the production of liner board is considered to have commercial possibilities.

Cooking with water or steam alone is well established as a commercial method but full information on the effect of different variables on the process has not been published. J. N. McGovern, K. J. Brown and W. A. Kraske[28] have followed the effects of cooking time, temperature, ratio of water to wood and wood moisture, in a process which consisted of subjecting aspen chips to steam or water cooking, followed by mechanical treatment at atmospheric pressure. The maximum strengths were exhibited by pulps produced in yields of 80–85%, irrespective of the pulping conditions. Both water- and steam-cooked pulps falling within this yield range were made into corrugating board equalling or approaching the strength properties of commercial hardwood semi-chemical pulps.

Alkaline pulping processes.—A very comprehensive and up-to-date summary of developments in this field is to be found in the reports for 1947 and 1948 compiled by S. D. Wells[29,30] for the Alkaline Pulping Committee of TAPPI.

E. Hägglund[31] has summarized the work which he and his colleagues have carried out on the role of sodium sulphide in the sulphate process. The mechanism is thought to involve the replacement of hydroxyl in the lignin by a mercaptan group which is then converted into a sulphide by reacting with a hydroxyl group in either the same or another lignin molecule.

J. Richter[32] has given an account of the development of the Kamyr continuous kraft cooking process which has been successfully operated on an 8-ton/day pilot-plant scale. The chips are first steamed in a separate unit to remove air and then pass, by means of a specially designed rotating feeding chamber, to the top of a 40-ft. high digestion tower. The chips move slowly down the tower, in the upper part of which they are impregnated at 100–120° c. In the centre of the tower the temperature reaches 165–170° c. and the wood is cooked for 1–2 hr. before being blown from the bottom of the tower. Steam formation in the digester is avoided by applying a hydraulic pressure about 30 lb./in.^{2} higher than the steam pressure at 170° c. The advantages offered by the process are the production of high-quality pulp for a steam consumption of less than 2000 lb./ton, increased output per unit of digester space, reduction of digester corrosion owing to the exclusion of air, and improved control of the process.

W. Overbeck[33] has found that whereas pre-hydrolysis, whether with water, dilute sulphuric acid or with buffered acid, does not in itself cause a loss of cellulose, it induces an increase in the cellulose loss in the subsequent pulping reaction. Thus, when untreated beech was cooked by the sulphate process the cellulose loss amounted to 1%, but the cellulose loss in the digestion of pre-hydrolysed beech reached 9%.

As regards by-products from the sulphate process, the possible value of alkali lignin as an alternative to carbon black for the reinforcement of rubber has been mentioned in an earlier Report. In this connexion, R. A. V. Raff, G. H. Tomlinson, T. L. Davies and W. H. Watson[34] have stated that better results are obtained with GR-S rubber if the lignin is subjected to an oxidation treatment. E. E. Harris, J. F. Saeman and

C. B. Bergstrom[35] have studied the pressure hydrogenation of lignin from black liquor and have obtained a yield of about 70% of volatile products.

Chromatographic methods are recommended by W. Jensen[36] on the grounds of rapidity and accuracy, both for the determination of the neutral constituents and for the complete analysis of tall oil. An improved method for the separation of the fatty and resin acids has been proposed by A. Linder and V. Persson.[37]

Sulphite process.—The theories of E. Hägglund and other Swedish workers on the chemistry of the sulphite pulping reaction have been summarized by H. Erdtman.[38,39] The reaction is considered to proceed according to the following mechanism. In the first stage the lignin in the wood is sulphonated by the substitution of hydroxyl groups to produce an insoluble lignosulphonic acid of high molecular weight. This sulphonated wood acts as a cation exchanger and removes calcium ion from the cooking liquor which becomes correspondingly more acid. In the next phase acetal linkages bonding lignin molecules to each other or lignin to carbohydrate are hydrolysed and further sulphonic acid groups introduced to produce soluble lignosulphonic acid of relatively low molecular weight.

The properties and method of isolating a new crystalline compound, 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavanone, from Douglas fir heartwood has been described by J. C. Pew,[40] who has also demonstrated that the presence of this flavanone is one of the main factors responsible for the resistance of Douglas fir to sulphite pulping. H. Erdtman[41] has also reviewed the researches of Hägglund on the isolation of the substances conferring resistance to sulphite pulping to pine heartwood. These substances, which were isolated by the acetone extraction of wood from which the resins had been removed by a previous extraction with ether or benzene, proved to be new phenolic bodies designated pinosylvin and pinosylvin methyl ether. They are assumed to inhibit the sulphite reaction by condensing with lignin to form large molecules which do not yield soluble products in the sulphite cook.

G. A. Richter[42] has carried out experiments on the factors influencing the sulphite cooking of western hemlock and has undertaken a large number of experimental two-stage cooks in which pulping with 15% sulphur dioxide solution or with bisulphite cooking liquor containing 8% free and 1% combined SO_2 was preceded by cooking with a range of different reagents. Pre-cooking with water and with all other reagents except sodium sulphite or bisulphite conferred resistance to delignification in the subsequent pulping reaction. Moreover, delignification became increasingly difficult as the temperature of the pre-cook was raised. Pre-cooking with 1% sulphur dioxide was outstanding in rendering the lignin inert. On the other hand, when the first stage consisted of a cook with 20% sodium sulphite at 130° c., a second stage cook with sulphur dioxide solution had a very specific delignifying action.

Details have been given of the process used in the new Weyerhauser mill at Long View which has been designed to produce 275 tons of bleached pulp per day by the magnesium bisulphite process.[43,44] The chips are digested for 8 hours in digesters of 35 tons (air dry wood) capacity and,

after dumping and washing, the spent liquor of 12–14% solids content is evaporated to 50–55% solids in quintuple-effect, stainless steel evaporators. The concentrate is then burned as a fuel. The magnesium oxide and sulphur dioxide produced are recombined to give a weak magnesium bisulphite solution which, after fortification, provides a regenerated cooking liquor.

Probably the only method of utilizing the total volume of waste liquor from the sulphite pulping industry is by the burning of the concentrated waste as fuel. There are, however, considerable technical obstacles to the development of an efficient and economic process. A report by W. T. Butler[45] to the Waste Committee of the Technical Section of the Canadian Pulp and Paper Association provides an excellent review of the literature on the evaporation and burning of calcium-base sulphite liquor and incorporates abstracts of papers dealing with existing commercial processes, viz. the Rosenblad, Ramén and Howard systems. One of the main difficulties in evaporation is to avoid the deposition on heat-transfer surfaces of a hard scale of calcium sulphate which quickly reduces thermal efficiency. The conditions controlling the precipitation of calcium sulphate from waste liquors have been studied by O. Samuelson.[46] L. R. Beath and H. S. Hill[47] have sought to overcome this scale problem by designing an electrical evaporator in which the current is passed through the incoming jet of waste liquor. A pilot plant has operated successfully, evaporating up to 2½ tons of water per day to yield a concentrate of 50–60% solids content. The process is considered economic where secondary electric power is available and the concentrated waste is burned for fuel. The scale problem is also said to be overcome in a thermal compression evaporator developed by H. L. Smith.[48] The spray-drying of sulphite waste liquor has been studied by H. H. Fogler, F. Herbolzheimer, R. M. Stinchfield and L. C. Jenness.[49]

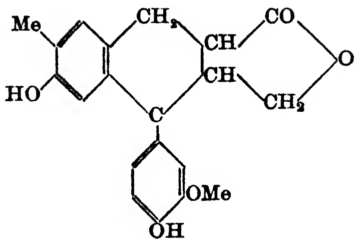
Sulphite waste has more limited uses in numerous other fields. As the result of trials extending over five years on the use of waste for irrigation, R. E. Stephenson and W. B. Bollen[50] have reached the conclusion that up to 60 tons per acre can be consumed annually in dilution with irrigation water without harmful effects either on soil or crops.

A new plant is being erected in Canada to produce 9000 gal. of alcohol a day from the fermentation of waste sulphite liquor.[51] A novel feature of this installation is the utilization of the carbon dioxide from the fermentation tanks for the manufacture of magnesium carbonate in an adjacent plant making magnesia/asbestos insulating slabs and piping. By a procedure which suppresses the formation of acetaldehyde during the fermentation of sulphite waste, J. Sundman[52] has increased alcohol yields by 4%. The influence of other substances inhibiting fermentation, viz. titratable sulphur dioxide and furfuraldehyde as well as acetaldehyde, has been investigated by G. O. Gadd.[53] E. W. Scripture[54] reports that the residual liquor, after the fermentation of the sugars for alcohol, is an excellent dispersing agent for cement.

By the pressure hydrogenation of alkaline sulphite waste liquor at 350° c. and 340–380 atm. initial hydrogen pressure, in a vessel of V2A steel which catalyses the reaction, W. Stumpf[55] has obtained neutral products, phenols and acids in proportions which vary according to the

lignin/sodium hydroxide ratio. The hydrogenation of lignin is also the subject of U.S.P. 2,390,063. Literature on the oxidation of sulphite waste has been reviewed by J. A. F. Gardener.[56] The utilization of sulphite waste liquor as a tanning agent has been covered by a survey undertaken by A. M. Johnson and H. B. Marshall.[57]

H. B. Lackey, W. W. Moyer and W. M. Hearon[58] describe a new and simple method for the isolation of conidendrin :—



from waste liquors from the sulphite pulping of western hemlock. The compound is precipitated by the addition of a small amount of an organic liquid such as trichloroethylene. The method has been applied on a semi-works scale in a plant producing 1 lb. of conidendrin per day.

Bleaching.—The multistage bleaching of kraft pulp with chlorine solution has been studied by J. L. McCarthy and H. Hibbert[59] who have investigated in detail the influence of temperature and p_H and the effect of the distribution of chlorine between the stages. The peroxide bleaching of groundwood is now being practised commercially on an extensive scale ; indeed, J. S. Reichert and R. H. Pete[60] have stated that, in U.S.A., expansion of the process is restricted only by the availability of peroxide to the pulp and paper industry. These workers have provided information on the effect of the different variables in the process and have recommended mill procedures for peroxide bleaching.

Zinc hydrosulphite is another bleaching agent for groundwood which is used chiefly for the brightening of the coloured Pacific Coast woods to render them acceptable for newsprint manufacture. The lay-out of a mill employing this process has been described by I. H. Andrews.[61]

R. M. Kingsbury, F. A. Simmonds and E. S. Lewis[62] have continued their investigation on the bleaching of groundwood with strongly alkaline hypochlorite solution at low consistency and low temperature. As the result of trials covering a number of North American woods, the process has been found to be satisfactory for hardwoods which, using 10% available chlorine, can in general be brought into the brightness range of 70–79%. Less satisfactory results were obtained when this method was applied to the bleaching of softwoods.

G. R. Gustafsson[63] reports that the oxidation of sulphite dissolving pulp during the final bleach depends chiefly on the p_H during that stage. At a p_H of about 10 a pulp with a low copper number, a high carboxyl number, high α-cellulose and good whiteness is obtained.

Paper making

Beating.—E. Hägglund and B. Webjörn[64] have examined the relationship between chemical composition and beatability and have shown that the response to beating cannot be judged from lignin content alone but is related to the percentage of low molecular weight hemicelluloses. Residual lignin may be of importance if it renders these hemicelluloses non-available. The relationship between the hemicellulose content and the physical properties of bleached kraft pulps has also been the subject of a research by F. T. Ratliff.[65]

O. Imselt[66] emphasizes that two effects should be considered in beating, one due to the edges and the other to the working surfaces of the bars. After attempting to find a correlation between mill beating and refining and various laboratory beating equipments, A. J. Laugher[67] also considers that a laboratory beater must be designed with bars if reasonable correlation with mill bar-type beaters and refiners is to be secured.

The 'Curlator,' a refiner with a novel type of action has been described by F. P. Silver.[68] The 'Curlator' converts the stock into nodules of 15–20% consistency which are subjected to a rolling treatment under light pressure, not exceeding 15 lb./in.^{2}, between two roughened surfaces. Under this action the fibres become permanently bent, kinked and twisted, acquire a rounder cross section and are freed from shives. The machine is at present finding application for the treatment of 30–45 tons per day of screening rejects in a newsprint sulphite pulp mill, where it has enabled a more shivy, higher-yielding pulp to be used. According to H. S. Hill, J. Edwards and L. R. Beath,[69] it should find numerous uses since it introduces new combinations of pulp properties and widens the range of qualities which can be obtained from a given pulp.

Sizing.—Aluminium chloride has not hitherto found application in the rosin sizing of paper as it is more expensive than alum; but C. C. Porter and W. H. Lane[70] have pointed out that it is widely used in the chemical and petroleum industries and is potentially available as a by-product in the form of a concentrated aqueous solution which, however, often contains traces of organic compounds. Trials with an aluminium chloride solution arising from the synthesis of ethylbenzene have shown satisfactory sizing with improvement in colour in a mill making kraft specialities; no increase in corrosion was observed. Aluminium chloride has, moreover, an important advantage in the manufacture of wet strength papers when melamine–formaldehyde resin is used. By using aluminium chloride, essentially the same wet strength properties can be obtained with 1% of m/f resin as resulted from 2½% of resin in the presence of alum.

L. Timgreen[71] reports that a saving of 65% in alum consumption has been secured by the use of sulphuric acid for the neutralization of the pulp in a mill using wet kraft pulp. O. Brauns[72] has found that by dissolving 0·2–0·4% of alum, on the weight of the pulp, in the beater before the addition of the rosin, optimum sizing effect was obtained, regardless of the nature of the pulp, the water used or the final p_H.

By means of three tests which he has proposed for measuring sizing, W. S. Wilson[73] has found that sizing gives less improvement to heavily beaten than to lightly beaten pulps—a phenomenon which he explains

on the assumption that, whereas rosin sizing renders the exterior surfaces of unbeaten fibres completely hydrophobic, the relatively large rosin particles are incapable of adhering to the small fibrils formed during beating. Possible substitutes and extenders for rosin have been considered by H. Wilfinger.[74] A highly condensed urea resin was considered to be the most promising extender and can replace up to 50% of the rosin.

By the oxidation of guar mucilage in the presence of borax, A. J. Haug[75] has prepared a tub-sizing adhesive which has given good results with rag paper.

Slime control.—The use of toxic chemicals for the control of slime in pulp and paper mills has greatly increased during recent years and three-quarters of the mills in U.S.A. are now said to be using such methods. Unfortunately, a great deal of published information deals with proprietary preparations, the compositions of which are not always fully disclosed. However, either organo-mercurials, particularly phenyl mercuric acetate, or chlorinated phenols or mixtures of these two types of toxicant, continue to be the agents chiefly used. Chlorination of fresh water supplies is also helpful in dealing with slime infection and N. S. Chamberlin and R. B. Martin[76] recommend that, when heavy infection is suspected, chlorination should be such as to reach a minimum of 0·2–0·5 p.p.m. of free chlorine residues throughout the system. Periodic flushing of the screening system with alkaline calcium hypochlorite solution has been found convenient and effective in a sulphite pulp mill. C. H. Rogers[77] suggests the use of Vancide 32, an aqueous solution containing 40% of 2′-hydroxyethylpyridinium-2-benzthiazyl sulphite, where a non-toxic agent is required, e.g. in mills making food-wrappings. Equipment for the feeding of toxicants into the mill system has been described by C. W. Dean.[78]

A method for the bio-assay of organo-mercurial slime control agents has been developed by B. F. Shema, J. B. Anderson and J. W. Appling[79] and used for the determination of the concentration of biologically active agent at various points in the mill, and for comparing the effectiveness of different dosage rates. The method, which depends on the measurement of the diameter of the zone of inhibition produced by a known quantity of the toxicant on the growth of *Sarcina lutea* I.P.C. No. 861, on agar, has been criticized by S. J. Buckman, who considers that the differences between the test conditions and those obtaining in the mill make interpretation of the results very difficult.

A problem somewhat related to slime control is the preservation of pulp against microbiological degradation; wet mechanical pulp is particularly susceptible to attack during storage. Mould infection of mechanical pulp is liable to cause a deterioration in colour, to induce slime in the paper mill system, to give rise to a high screening loss and, if attack is severe, to cause loss of fibre by decay. The preservation of mechanical pulp by the application of a fungicide on the lap machine is therefore often practised. According to B. F. Shema,[80] moist mechanical pulp can be kept free from microbiological attack for 12 months, if not less than 0·14% of sodium pentachlorphenate on the weight of the pulp, is applied at the top press roll. S. J. Buckman[81] holds the view

that it is more advantageous to close the white water system as far as possible, to operate at a high pit-temperature and to add a preservative containing phenyl mercuric acetate to the white water. By this method not only was the pulp preserved for storage but the pulp mill system was maintained free from slime. Only one organism, and that without any significant influence on pulp quality, was found to develop in the stored pulp. This mould, which was subsequently identified as *Penicillium roqueforti* Thom, has been found by J. W. Appling, S. J. Buckman and R. N. Meals[82] to possess exceptional resistance to phenyl mercuric acetate.

Pitch.—There has hitherto been a conflict of evidence on the relationship between hardness of mill water and liability to pitch troubles. The explanation of these apparently conflicting experiences may be found in the work of G. Gavelin,[83] who has provided experimental evidence to support the view that the precipitation of pitch is dependent, not on hardness, but upon the bicarbonate ion content of the mill water. In a subsequent paper,[84] this author confirms the efficiency of hexametaphosphate in the control of pitch, when added to the white water at 0·05% on the weight of the paper. An investigation of the mechanism of the process has shown that it could be attributed neither to the removal of calcium ions nor to the stabilization of the pitch emulsion. It was thought to be connected with the property, which hexametaphosphate solutions are known to possess under certain conditions, of depositing corrosion-protecting films on metals. It was considered that these films might also be effective in preventing the adhesion of pitch.

The foaming of wood pulp suspensions has been discussed by S. V. Sergeant.[85,86]

The paper machine.—The design and operation of suction couch and suction press rolls have been discussed by R. C. Heys.[87] The performance of the riffler in the removal of dirt from a stock produced from mixed waste paper has been the subject of an investigation by S. F. Smith.[88] By means of a series of surface baffles arranged vertically above the normal bottom dams it was found that light dirt could be almost completely (97%) removed. Most of the heavy dirt was also eliminated; on an average 75% was removed.

Gas-fired radiant-heat dryers have been advocated by G. W. Garland[89] as a means of increasing the drying capacity of existing machines, while keeping alterations and installation costs to a minimum.

I. H. Peters[90] has described the application of the Kenwood wheel, a simple device for measuring the elongation of felt, where, as for example with the bottom felt of a board machine, a felt is used for power transmission and is liable to be over-stretched.

In save-all systems depending on the aggregation of fibres, B. Ekholm[91] has suggested that sodium pectate is superior to rosin size.

Wet-strength paper.—Little new work of importance has been published during the year on the use of urea–formaldehyde or melamine–formaldehyde, the resins chiefly used commercially for the production of paper of improved wet strength. Reference to the effect of polyethyleneimine in improving wet strength is made by H. Wilfinger,[92] who states that 1–2% of this polymer is effective and that it operates under alkaline conditions.

Coating.—Information on the improvement of clay coatings by the incorporation of titanium pigments has been given by W. R. Willets.[93] Titanium calcium pigment, produced by the co-precipitation of a mixture of 30% of rutile titanium dioxide and 70% calcium sulphate anhydrite, improves brightness, colour and opacity. About 2·5 parts of this pigment is equivalent to 1 part of anatase titanium dioxide.

Hydroxyethyl cellulose has been reported by D. R. Erickson[94] to be of special interest as a coating adhesive for clay or other pigments in machine coating processes. The hydroxyethyl cellulose is dissolved in caustic soda solution from which it is precipitated as a non-tacky solid. An advantage claimed for the use of this material is that a satisfactory printing surface can be obtained without the need for super-calendering, with its attendant disadvantages.

De-inking.—Methods of alkali de-inking have been reviewed by R. Carr,[95] who mentions that modern printing inks require a stronger alkaline treatment. E. W. Turley[96] recommends the use of sodium silicate in conjunction with caustic soda and peroxide for the de-inking of newsprint. The Zundel process for the de-inking of newsprint by the use of an alkaline extract of coniferous bark has been described by R. S. Aries.[97]

Testing and analysis

Pulp testing.—Revised and more precise rules for the sampling and testing of wood pulp for moisture content have been approved by the British and Scandinavian pulp and paper industries.

Investigations of laboratory beating equipment, carried out by W. E. Cohen,[98] have shown fairly satisfactory agreement between three different Lampén mills. A wide difference was observed between the results obtained with the Lampén mill and with the Clark Kollergang. Two of these latter equipments were not in close agreement. Cohen found that the presence of dissolved salts in the water used in beating experiments exercises a marked effect; he therefore proposes that identical bulk rather than freeness values should be made the basis for comparing different pulps, as bulk is less sensitive to differences in the water supply. C. E. Hrubesky[99] has extended his comparison of freeness testers to include figures for the Williams precision model. Values for the 15 board stocks examined failed to reveal any correlation between the Williams and other freeness testers included in this study.

A rapid method for the evaluation of pulps for insulating board manufacture has been put forward by H. Z. Mohrer, J. H. Conover and O. W. Frost[100]; by using radiant heat in addition to hot circulating air, hand sheets 6 in. in diameter and weighing 14–17 g. can be dried in 10–12 min.

Paper testing.—A large number of papers on this subject has been published during the year, of which it is possible to mention only a selection.

PATRA has issued a tentative standard method[101] for determining water-vapour permeability under temperate and tropical conditions. Gravimetric methods, such as that described by PATRA, are not readily applicable to the measurements at low temperatures owing to the extremely low permeability values which are then obtained. This difficulty is

overcome in a sweep gas method devised by W. A. Wink and L. R. Dearth,[102] in which the required sensitivity is achieved by the use of a very small electric hygrometer.

In the field of mechanical testing, attention is drawn to the work of N. G. M. Tuck and S. G. Mason[103] on certain factors influencing the accuracy of Mullen bursting-strength testers. The standardization of gauge expansibility is considered desirable and, if a high degree of accuracy is sought for, the gauge should be calibrated under dynamic loading conditions. The presence of air constitutes another source of error. A simple method for detecting air is described; the use of ethylene glycol is preferred to glycerol as it facilitates the removal of air. B. Steenberg[104] has given an account of his latest work on the rheology of paper and H. F. Rance[105] has considered the relationship between folding endurance and elastic flexibility.

Several useful papers have been concerned with the evaluation of mould resistance. G. A. Cruickshank[106] has demonstrated that, in the agar plate method frequently adopted for the assessment of the mould resistance of paper, the bleaching and diluting effect of the agar on the antimycotic agent in the paper may seriously influence the result, particularly with light-substance papers. He, therefore, proposes that the volume of agar should be adjusted according to the thickness of the paper under examination. The choice of the test organism, the p_H of the agar and the duration of the test are other factors which have an important effect. J. W. Appling, S. J. Buckman and C. D. Cash[107] take the view that, even with the above-mentioned modification, the use of agar is open to the objection that it involves testing under conditions which are unrelated to the most severe tests which are likely to be encountered in actual use. They prefer to employ a technique in which the paper specimen is moistened with a neutral nutrient salt solution.

The Bausch and Lomb and the Sheen Glossmeters have been compared by V. G. W. Harrison[108] who found important discrepancies between the visual and the glossmeter grading of nine printing papers. The best results were obtained when the angles of incidence and viewing were 45°. The relationship between the specific surface of a pulp, determined by d'A. Clark's method, and the scattering coefficient of hand-made sheets made from it, has been studied by L. Nordman.[109] J. A. Van den Akker[110] proposes that, in the application of the Kubelka–Munk theory, thickness, which is not a convenient variable, should be replaced by basis weight, in g./cm.^{2}, to yield the 'specific scattering coefficient' and the 'specific absorption coefficient.'

References

1 *Paper Mkr., Lond.*, 1949, **118**, 242
2 U.S. Dept. Agriculture, Yearbook of Agriculture; **Trees, 1949, 153**
3 *Industr. Chem. chem. Mfr.*, 1948, **24**, 545
4 *TAPPI*, **1949, 32, 534**
5 **Ibid., 563**
6 **Ibid., 79**
7 *Paper Tr. J.*, **1949, 128,** *Industr. devel. Sect.*, **13**
8 *TAPPI*, **1949, 32, 393**
9 **Ibid., 494**
10 *Svensk Papperstidning*, **1949, 52**, 493

[11] *TAPPI*, 1949, **32**, 145
[12] Ibid., 91
[13] Ibid., 319
[14] *Pulp Pap. (Mag.), Can.*, 1949, **50**, No. 8, 128
[15] *TAPPI*, 1949, **32**, 58
[16] Ibid., 337
[17] *Pulp Pap. (Mag.), Can.*, 1949, **50**, No. 3, 215
[18] Ibid., No. 12, 101
[19] *Finnish Pap. Timber J.*, 1949, **30**, No. 21, 383
[20] Ibid., 1946, **28**, No. 13, 200
[21] *TAPPI*, 1949, **32**, 67
[22] Ibid., 29
[23] Ibid., 150
[24] *Das Papier*, 1948, **2**, 437
[25] *Pulp Pap. (Mag.), Can.*, 1949, **50**, No. 9, 65
[26] *TAPPI*, 1949, **32**, 400
[27] Ibid., 179
[28] Ibid., 440
[29] Ibid., No. 6, 35A
[30] Ibid., No. 12, 36A
[31] Ibid., 241
[32] Ibid., 330
[33] *Angew. Chem.*, 1949, **61**, 219
[34] *Rubb. Age, Lond.*, 1948, **64**, 197
[35] *Ind. Eng. Chem.*, 1949, **41**, 2063
[36] *Finnish Pap. Timber J.*, 1949, **31**, No. 12, 225; No. 16, 293
[37] *Svensk Papperstidning*, 1949, **52**, 331
[38] *TAPPI*, 1949, **32**, 75
[39] Ibid., 346
[40] Ibid., 39
[41] Ibid., 303
[42] Ibid., 553
[43] *Pulp Pap. Ind.*, 1948, **22**, No. 12, 38
[44] *Chem. Engng.*, 1949, **56**, No. 2, 137
[45] *Pulp Pap. (Mag.), Can.*, 1949, **50**, No. 11, 108
[46] *Svensk Papperstidning*, 1949, **52**, 283
[47] *Pulp Pap. (Mag.), Can.*, 1949, **50**, No. 8, 89
[48] Ibid., No. 9, 84
[49] *TAPPI*, 1949, **32**, 389
[50] Ibid., 422
[51] *Pulp Pap. Ind.*, 1949, **23**, No. 9, 44
[52] *Finnish Pap. Timber J.*, 1949, **31**, No. 17, 309
[53] Ibid., 1946, **28**, No. 7A, 61
[54] *Paper Tr. J.*, 1949, **129**, No. 17, 33
[55] *Angew. Chem.*, 1949, **61**, 400
[56] *Pulp Pap. (Mag.), Can.*, 1949, **50**, No. 9, 102
[57] Ibid., No. 8, 98
[58] *TAPPI*, 1949, **32**, 469
[59] *Pulp Pap. (Mag.), Can.*, 1949, **50**, No. 5, 88
[60] *TAPPI*, 1949, **32**, 97
[61] Ibid., 286
[62] Ibid., 273
[63] *Finnish Pap. Timber J.*, 1949, **31**, No. 17, 308
[64] *Svensk Papperstidning*, 1949, **52**, 131
[65] *TAPPI*, 1949, **32**, 357
[66] *Norsk Skogindustri*, 1949, **3**, 145
[67] *Aust. Pulp. Pap. Ind. tech. Ass. Proc.*, 1948, **2**, 155
[68] *Paper Tr. J.*, 1949, **128**, *Industr. devel. Sect.*, 75
[69] *Pulp Pap. (Mag.), Can.*, 1949, **50**, No. 3, 153
[70] *TAPPI*, 1949, **32**, 465
[71] *Finnish Pap. Timber J.*, 1946, **28**, No. 7A, 72
[72] *Svensk Papperstidning*, 1949, **52**, 579

[73] *TAPPI*, 1949, **32**, 429
[74] *Neue dtsch. Papier Ztg.*, 1949, **3**, No. 3, 86
[75] *TAPPI*, 1949, **32**, 410
[76] *Pulp Pap. (Mag.), Can.*, 1949, **50**, No. 8, 105
[77] *Paper Mill News*, 1949, **72**, No. 11, 24
[78] *TAPPI*, 1949, **32**, 419
[79] Ibid., 489
[80] Ibid., 227
[81] Ibid., 129
[82] Ibid, 300
[83] *Pulp Pap. (Mag.), Can.*, 1949, **50**, No. 2, 59
[84] Ibid., No. 10, 108
[85] *Paper Mkr., Lond.*, 1949, **117**, 411
[86] Ibid., 1949, **118**, 32
[87] Ibid., 1949, Midsummer No., 34
[88] *Proc. Papermkrs' Ass.*, 1948, **29**, Part 2, 477
[89] *TAPPI*, 1949, **32**, 277
[90] Ibid., 229
[91] *Svensk Papperstidning*, 1949, **52**, 227
[92] *Papier, Darmstadt*, 1948, **2**, 265
[93] *TAPPI*, 1949, **32**, 349
[94] Ibid., 289
[95] *Paper Ind. & World*, 1949, **31**, 337
[96] Ibid., 340
[97] *Paper Tr. J.*, 1949, **128**, No. 26, 23
[98] *Aust. Pulp. Pap. Ind. Tech. Ass. Proc.*, 1948, **2**, 118.
[99] *TAPPI*, 1949, **32**, 315
[100] Ibid., 569
[101] PATRA Packing Research Report No. 2, 1948
[102] *TAPPI*, 1949, **32**, 232
[103] *Pulp Pap. (Mag.), Can.*, 1949, **50**, No. 3, 132
[104] Ibid., 207
[105] *Paper Mkr., Lond.*, 1949, Midsummer No., 22
[106] *TAPPI*, 1949, **32**, 370
[107] Ibid., 427
[108] *Paper Mkr., Lond.*, 1949, **118**, 106
[109] *Svensk Papperstidning*, 1949, **52**, 441
[110] *TAPPI*, 1949, **32**, 498

CELLULOSE TEXTILE CHEMISTRY

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THE present year has been marked by a very substantial detailed activity in research, development and organization in all branches of textile chemistry, based primarily on the utilization of cellulosic textile fibres. From the volume of work published and discussed, it cannot be said that there has been a great deal of new development, and, of course, innovation of this kind is becoming increasingly difficult as exploration has already ranged very widely.

A great deal of work is still being done on the molecular structure of cellulose; on the physical structure of its fibre forms, with the aid of a very wide variety of physical techniques: on the chemical structure, preparation and properties of derivatives; and on the reactions of cellulose in many different chemical environments. The textile processer has previously been interested in this work because it throws increasing light on the mechanical behaviour of fibres and defines the limits of safe processing conditions. But now he is also interested as it provides new information by which dyeing mechanisms can be studied and new dyeing and finishing procedures can be devised. The increasing number of new cellulose derivatives which are becoming available as plastics is also of great interest to the finisher. Whereas ester and ether derivatives are still the most important, there are indications that modifications of cellulose produced by oxidation are likely to become more widely used industrially in the future.

The increasing range of investigations on the structure and reactional properties of other high-molecular carbohydrates is also of great interest in textile chemistry. They provide collateral information about the structure and reactions of fibrous cellulose itself, and in addition they are likely to lead to developments of immediate industrial importance such as the provision of new printing thickeners, new finishing agents, new sizing materials and the like.

Although a very large number of finishing procedures have been suggested and described it is interesting to find that a surprisingly high proportion of them are not concerned primarily with modifications in the mechanical and optical properties of fabrics—accepted generally as the chief aims of finishing—but with proofing operations. As regards the protein fibres, dealt with elsewhere, this fact is illustrated by the large number of substances still being proposed for the prevention of insect attack. The counterpart for cellulosic textiles is protection against micro-organisms, and greatest emphasis is laid on bacterial attack and its prevention (rot proofing). Treatments for all classes of fibre, to confer resistance to wetting, have been very numerous.

Essentially new information on dyeing, either fundamental or applied, has not been very plentiful although many details which were missing from such work in previous years have now been supplied. The general course

of development has been in the direction of speed and continuous working. This has, of necessity, to start with improvements in machinery design, but it has meant also new and sometimes unorthodox dyeing conditions and sequences of processes, so that parallel investigations have often been required to determine the behaviour of dyes and of fibres in these new conditions.

The design of processing machinery in general is in a transitional stage. Manufacturers in this and other countries are making machines out of more satisfactory materials; they are improving the versatility of given units, increasing the ease and accuracy of control, paying more attention to the efficiency of devices for circulating liquors, steam, and hot air, and improving economy in steam and power. Nevertheless, with one or two exceptions, the general design of individual machines and the lay-out of plants continue to follow broadly orthodox lines. This may change in some countries with the experience that is now becoming available, in the high-speed, continuous processes just mentioned.

The organization of research and development remains very similar to that of immediately precedent years. The majority of patents for processes come from the technical research and development departments of the large chemical manufacturing firms and application-research owes more perhaps to this source than any other. Applied departments of universities and technical colleges have become increasingly ambitious in the examination of the fundamental mechanisms of textile processes. Of the three industrial research associations in this country dealing with cellulosic textiles, the Shirley Institute publications have this year been rather heavily weighted in the direction of spinning, manufacturing and physical testing, as compared with the finishing sections, whereas the Rayon Research Association is not yet in production as far as outside publication is concerned.

The practice adopted a few years ago by the American Association of Textile Chemists and Colorists of concerted investigation, on a competitive sectional basis, of important technical problems in dyeing and other branches of processing has led occasionally to fairly rapid increase in the understanding of the conditions in which new procedures may operate efficiently. Each subject is fairly narrowly restricted in scope and the cooperation of a number of workers from the technical staffs of member firms ensures that the planning of the campaign and the assessment of the results is effected with a full regard to industrial operation. Some of these investigations will be referred to later. There is no comparable scheme in this country, the closest analogue being the technical committees of societies such as the Dyers and Colourists and the Textile Institute, and their terms of reference are generally wider in scope. It is unlikely that technical circles as a whole would welcome the competitive element, but some version of the scheme might prove an encouragement to younger scientific and technical workers.

The dichotomy of the trained investigator from the man in the works, and of laboratory investigation from bulk processing of goods is already marked in many regions of textile activity. It is likely to increase with the present inevitable tendency to dig deeper into fundamental causes and to record and discuss the results in the terminology of science.

The delay which occurs in the general adoption of new and carefully examined ideas by the working sections of the industry has already been the cause of grave concern among the more enterprising scientists and industrialists. The matter is an urgent one in this and in many other countries of the world for whom efficiency in industrial production and distribution is now so vital a necessity. Something is being done in many places to spread the news and to break down prejudices. Even a definition of the problem is valuable. It is encouraging to know therefore that the Annual Conference of the Textile Institute in Dublin[1] this year devoted its sessions to a consideration of the industrial application of new knowledge. It is true that many of the contributions consisted of examples of this application to special problems, but there were also a number of discussions on how to improve the machinery of liaison between the scientist, the industrial technologist, and the managerial staffs of the textile industries.

The Society of Dyers and Colourists has been responsible, on two previous occasions since the close of the war, for extremely valuable symposia at which were discussed, at levels ranging from the purely fundamental to the completely practical, groups of subjects of vital interest in the industrial chemistry of textiles. Each of these symposia has been of great assistance in bringing together diffusely scattered information with a common significance and emphasizing how its various items were interrelated. The third such gathering at Harrogate[2] this year reached a very high level of quality and importance. The subject was photo-chemistry whose main applications are, of course, found in the problems of fading and tendering of dyed textiles on exposure to light. On this subject there exists recorded a very large body of information imperfectly unified by fundamental theory. It was encouraging to find so high a proportion of contributions from physical and organic chemists whose interest had not previously been specifically in the direction of tinctorial and textile applications. They must have seen in the phenomena discussed a fruitful field for the testing and extension of general theories of light action and light-initiated reactions.

On the practical side two further events should be recorded. The British Industries Fair, besides bringing together at Olympia an extraordinarily wide range of chemicals, dyes, measuring instruments etc. for the inspiration of the textile chemist, displayed at Earls Court an epitome of the great diversity in construction and design of British textile manufactures. It showed the high technical skill of our native printing industry and enabled some assessment to be made of the place to be occupied by the newer manufactured fibres. One exhibit, that of the Bleachers' Association Ltd., by taking the form of a control laboratory did a valuable service to the industry in bringing home to the general public the value of analytical control and investigation in the maintenance of high manufacturing quality.

The Textile Recorder Exhibition of Textile Machinery in Manchester, the first of its kind since the war, is to be counted a great success in terms of the number and quality of the exhibits and in the interest aroused, although it cannot be said to have done full justice to the textile-processing machinery now being designed and produced in this country.

One further, and most interesting event, was that arranged by the Calico Printers' Association Ltd. at Manchester on the occasion of the Association's jubilee year. Along with some exhibits to illustrate the importance of scientific investigation and control in the textile printing industry, the main exhibition was of printed styles produced by the company and its component firms in the past. As a lively and graphic display of the evolution of printed design it was most stimulating but to the technologist it also provided a striking object-lesson on the enormous widening in the range of effects made possible first by the development of the synthetic dye industry, and later by the manufactured fibres. At the one end of the exhibition were prints of the late eighteenth and early nineteenth centuries executed with a precision of engraving and a perfection of impression which would do justice to the best of modern printing, but in the dull and monotonous colour range which was all the great skill of the printers of that time could extract from the indigo, madder, dyewoods, and mineral dyes then available. The first prophetic note of clarity and brilliance was struck by the introduction of magenta, and thenceforward the extending palette of the colourist was illustrated in a most exciting fashion.

Cellulose

Natural fibres

Although much has been published during the year on the botany, genetics and culture of cellulose-fibre-bearing plants, the consideration of this material is, in general, remote from our special interest. Mention of one summary in this field should not however be withheld. E. Lord[3] has continued his surveys of previous years on the production and characteristics of the world's cotton crops, with a long, detailed account of the strains, cultivation, diseases and fibre characteristics of the cottons of the Sudan. In the series of articles appearing in the *Journal of the Textile Institute* on the structure of the principal varieties of textile fibre, D. A. Clibbens[4] has given an account of the cotton fibre; this account while intentionally simple and popular in treatment shows all the marks of lucidity, care and logical arrangement which distinguish the work of this authoritative writer. It may be recommended for the information of those to whom this subject is unfamiliar. Similar simple but authoritative statements are made by A. J. Turner[5] for the structure and composition of flax. The same writer[6] has considered the relation of structure to mechanical properties of the long bast fibres in the same way. S. Nagabhushana[7] as a result of measurements on a large number of cotton hairs has come to the conclusion that hairs attached to different parts of the seed vary significantly in fibre rigidity, ribbon width, and convolution frequency. These differences are ascribed to variations in the time taken by the epidermal cells on different parts of the seed to start the process of differentiation by which transformation into a hair is effected. L. E. Hessler, G. V. Merola and E. E. Berkley[8] have determined the degree of polymerization of cotton fibres at various stages of development (compare Preston and Middlebrook, *see* below) so that fibres consisting of little more than primary wall could be compared with those with a secondary wall of increasing proportions. The degree of

polymerization was in general much higher in the cellulose of the secondary wall, and it was shown that this could be due to the extreme sensitivity of the material in the primary wall to exposure to air and light. These studies were extended by Hessler, M. E. Simpson and Berkley[9] to include the relation of D.P. with fibre width, fibre length, convolution frequency and strength. K. Hess[10] has attempted to relate the rate of transport of building material, and the formation and deposition of cellulose with the topography of the natural hair. The speed of the reactions by which cellulose is formed is considered to be chiefly determined by two factors: (i) the large surface of the fibrils at which reaction occurs (favourable and (ii) the enclosing action of the primary wall which limits the volume of transporting fluid able to pass in unit time and to make contact with the fibril surfaces. W. K. Farr[11] has also considered the mechanism of secondary wall formation in vegetable fibres. Evidence is given that a membrane (tertiary wall) is formed between the fluid transporting the cell-building materials and the inner (formative) surfaces of the secondary wall. Collection and organization of the fibre substance are traced to various parts of the fibre and the organization appears to occur in this tertiary wall before the fibrillated cellulose is deposited on the growing surface of the secondary layer. An interesting statement is that little evidence of organization is found in the primary wall, and that the fibril formation and arrangment within the secondary layers does not appear to be controlled by the structure in this wall.

The well-known rotation test shows that the fibrils of jute are arranged in a Z or anti-clockwise helix. B. K. Chakravarti and C. R. Nodder[12] studied the differences between the mechanical properties of fibres twisted with and against this natural twist, during the process of spinning. Increase of the natural twist, as may be expected, reduces the resistance to further twisting, diminishes the fibre-bundle diameters and increases the stiffness of the fibre, whereas an imposed twist in the opposite direction tends to increase the tensile strength. M. K. Sen and H. J. Woods,[13] in the analysis of the jute fibre structure by X-ray diffraction methods, have been unable to find any evidence of a difference in the structure of jute cellulose from that of other fibres, and have shown that certain spacings characterizing this fibre may be ascribed to the lignin present. The structural inter-relations of the true cellulose with lignins and different constituents of the total hemicellulose content are discussed by P. B. Sarkar, H. Chatterjee, A. K. Mazumdar and K. B. Pal.[14,15] The lignins are thought to be combined with the polyuronide fractions of the hemicelluloses, and in the latter group the hexosans are shown to be the most easily removed and are assumed to play a great part in cementing the hemicelluloses to the crystalline cellulose regions. P. H. Hermans and M. K. Sen[16] attribute the high regain of jute as compared with that of other natural cellulosic materials to the uronide and hexose fractions of the fibre. Although of greater interest in the preparation of fibrous material for paper, the outline by K. Freudenberg[17] of the work carried out in Germany during the war in the isolation, characterization and determination of lignin structures will be of value also to those engaged in the preparation of lignified fibres for textile purposes, and as raw material for manufactured cellulosic fibres. A corresponding review by

G. Jayme[18] deals with the work done to extend the sources of technical celluloses. The differentiation of inner and outer fibre-cell walls through differences in the pitch and other details of arrangement of the respective molecular helices has been noted in a number of natural cellulosic fibres. R. D. Preston and M. Middlebrook,[19] examining sisal fibres by *X*-ray diffraction analysis and in the polarizing microscope have shown the presence of a diffuse helical arrangement of comparatively flat slope (40° to fibre axis) in the outer cell layer as compared with a more precise arrangement and a slope of 20° in the inner wall. Advantage was taken of the slow-growing habits of the plant to obtain examples of a wide range of development in the constituent cells, from those of immature growth consisting of little more than the primary wall, to those in which the secondary wall is fully developed.

One of the most complete pictures of a perfectly organized structure in natural cellulose has been obtained by R. D. Preston, E. Nicolai, R. Reed and A. Millard[20] for the vescicle wall of the seaweed *Valonia*, by electron microscope examination of casts of the structure shadowed by chromium deposition. The cellulose is in the form of extremely regular fibrils (diam. 300A.) arranged with regular intervening spaces and in almost perfect parallel array to form lamellae, the fibrils in one lamella being arranged at an angle just under 90° to those in the lamellae above and below. W. G. Kinsinger and C. W. Hock[21] have used a similar technique for fibrous celluloses and have shown the normal visible fibrils to consist of bundles of finer fibrils (90–400A. diam.). There is evidence of a recurrent discontinuity in the fine fibril arrangement at intervals of 150A. Electron micrography of a variety of bast fibres and cotton hairs carried out by K. Mühlethaler[22] has revealed an organized parallel fibrillar system in secondary walls, a network fibrillar system in primary walls and complete independence of cellulosic and non-cellulosic constituents.

Moisture relations of cellulosic fibres.—J. Crank (with M. E. Henry[23]) has extended his mathematical studies of the diffusion of dye particles into fibres, to a consideration of the uptake of moisture vapour by solid bodies of known form from a surrounding atmosphere. He has shown that close analogies exist between the two types of process and that similar mathematical treatments apply. The attainment of equilibrium conditions by different routes is considered and, in particular, the conditions which will lead to equilibrium in the shortest possible time are indicated. The work is of fundamental application in the industrial conditioning of fibrous substances in atmospheres containing specified amounts of water vapour.

M. Wahba,[24] in determining the heat of wetting of different varieties of fibrous cellulose with water and with other liquids, concludes that the rate of heat evolution is dependent upon the pore size of the fibre and the molecular complexity of the wetting liquid as well as the probable intermolecular forces between fibre and liquid. Heats of wetting with different liquids change in the same order as the relative extent to which the vapours are absorbed by cellulose. The experimentally determined specific heat-evolution on immersion is shown to agree quite closely with the calculated free energy of saturation.

The relations between water sorption and both inter- and intra-fibre restraints to swelling in assemblages of cellulosic fibres—natural in wood, artificial for paper and pulp—have been set out by W. Barkas.[25] He has devised equations which can be used to calculate the relations between vapour pressure, water content and volume swelling on the one hand and internal and applied restraints to swelling on the other. He puts forward the theory that absorption hysteresis is brought about by the action of these restraints. A part of this field is covered by J. A. Howsmon[26] who attempts to relate moisture regain with crystalline–amorphous ratio in the cellulose through an accessibility factor for the adsorbing groups of the cellulose molecule. S. H. Mhatre and J. M. Preston[27] have constructed an improved displacement densitometer for the accurate measurement of the density of fibres, while they are immersed in water or other liquids, as a means of measuring the sorption of the liquid. C. Legrand,[28] from X-ray studies of wet and dry ramie and cotton, claims to have demonstrated the fixation of water-molecules between the hydroxyl groups of the cellulose.

Water adsorbed on cellulose and cellulose derivatives is divided by G. Champeter and P. Clement[29] into two types. Calculations from measurements of water absorption are given which show that the only attracting sites within the fibre are at those hydrophilic groups which do not take part in intermolecular bonding. With cellulose, the number and accessibility of these sites limits the adsorption. With cellulose acetate the adsorption on immediately available sites is observed to be followed by a progressive loosening of hydrogen bonds between hydroxy and acetate groups, and further occupation of these liberated sites by water.

In studying the development of the cotton fibre there has of recent years been an accumulation of evidence to show that the convolutions are determined by an inherent spiral structure and are not formed at random by strains set up when the newly-formed turgid fibre dries out. R. D. Preston, A. B. Wardrop and E. Nicolai[30] have produced comparable evidence for the cellulose structure in two algae; they have shown that the molecular orientation in the dried algae is no different from that in algae that have been examined without ever having been dried. W. H. Rees[31] has shown that the initial heat of absorption of water by different forms of dried fibre is the same, but that differentiation occurs between one kind of fibre and another as the initial amount of water—before measuring heat of absorption of a further amount—is increased.

J. B. O'Sullivan[32] has continued his long series of studies on the conduction of electricity through cellulose, in the presence of electrolytes. The temperature coefficient of the conductivity appears to be independent of the kind or quantity of electrolyte at high moisture contents, and dependent only on the amount of water present. At low moisture contents, these relations are more complex and from the results obtained a theory is developed which depends on the presence of continuous and interrupted channels containing water within the cellulose.

Soda absorption and mercerization.—A fair amount of attention still continues to be given to the process of swelling with concentrated solutions of caustic alkalis and to the properties both of the swollen soda

cellulose, and of the mercerized cellulose. The latter consists principally of the hydrate form which remains after the soda cellulose has been decomposed by washing. The reality of compound formation between alkali and cellulose appears to be largely a matter of definition in that sodium ions take up a definite place in the lattice of the crystalline portions, but little direct evidence exists as to the forces which retain them. A. Bréguet, R. Viatte and H. Perra by measuring the water absorption accompanying absorption of soda at different alkali concentrations have compared the changes which take place in cotton cellulose[33] with those in regenerated cellulose fibres.[34] They differentiate sharply between a reversible swelling in the amorphous region (up to a concentration of 12·24% for cotton cellulose) and an irreversible swelling which takes place in the crystalline region for higher alkali concentrations. The separation between the two processes is marked by a maximum swelling at the critical concentration. For viscose there are two maxima at 9·3% and 13·97%. Irreversible swelling only occurs after the second maximum, reversible swelling in the amorphous region only before the first. As distinct from cotton, the swelling between the two maxima appears to be a superposition of the two kinds of swelling mechanism. This picture is amplified by E. Calvet[35] and by A. Jäger.[36] The latter examines critically the methods proposed by previous workers for investigating the cellulose–soda complex, and claims that in order to understand the complex formation between alkali and cellulose, it is also necessary to consider how the total water content in alkali-swollen fibres is distributed between free and bound water. Calvet, who used an interferometric method to measure absorption over the region 8–20% caustic soda concentration, states in partial contradiction of Bréguet *et al.*, that at both 15° C. and 40° C. absorption by native cellulose is reversible for all concentrations used. For cellulose previously mercerized the absorption is reversible at the higher temperature and irreversible at the lower. C. Legrand,[37] by *X*-ray diffraction methods, compares the lattice dimensions of dry hydrate-cellulose before and after swelling with those of water, and reports that the reiterated hydration increases the crystallinity of the material. The return from the hydrate to the native crystal arrangement when mercerized cellulose is heated with a dehydrating agent is said by T. Kubo and N. Nozuka[38] to be dependent upon the degree of polymerization, diminishing with shortening chain length. N. N. Saha[39,40] has examined the action of caustic soda solutions upon jute fibres over a wide range of concentration and temperature. Although the general picture is similar for other fibres there are important differences in the lattice spacings (101) as compared with ramie and in the ratio between native and hydrate cellulose as compared with cotton. E. Cerbaro[41] suggests that viscose fibres—particularly in staple fibre form which may be present in mixed yarns—can be identified by the changes in the disposition of the longitudinal striations produced by mercerization. These tend to move to a direction diagonal to the fibre axis and to become irregularly separated from each other. S. M. Edelstein[42] makes the interesting statement that cellulose fibres below 200μ. in length show an increased solubility in alkali solutions, and this gives an indication of the degree of comminution which is necessary before the

original fibre structure is radically interfered with. The same worker[43] has further examined the absorption of barium hydroxide under standardized condition to give a value called the 'barium number.' It is stated that an adequate differentiation is made between unmercerized cotton and cotton mercerized technically with different efficiencies and that the test is not affected by the presence of the dyes normally used to colour cotton. The first paper of Edelstein should be read in conjunction with a study by M. L. Nelson and C. M. Conrad,[44] who have also investigated the effect of grinding upon the structure of cotton cellulose. In this work the crystallinity and accessibility factors have been determined by measurements of the acid hydrolysis rates, the heat of wetting and the moisture absorption. The proportion of crystalline cellulose is shown by all methods to diminish with the severity of comminution, though the *X*-ray diffraction pattern of the surviving crystalline cellulose does not change. Moistening and drying the ground cellulose restores to some extent the disorganized crystalline arrangement.

Hydrolysis and oxidation of cellulose.—These reactions are in essence all degradative, and most of the work reported falls into one of three categories : (i) extension of studies of the rate both of hydrolytic and oxidative attack to obtain further information about the crystalline-amorphous ratio of fibres, (ii) oxidation applied as a means of increasing the available information on the constitution of the cellulose molecule, and (iii) studies of degradative attack occurring in use, during exposure to atmospheric influences, in processing, etc. T. Svedberg[45] made extensive studies of celluloses which he degraded in various ways, then nitrated and subjected to some of the various fractionating techniques in which he has particularly specialized; he showed that hydrolysis or ultrasonic waves tends to produce fractions within a narrow range of degrees of polymerization (about 100). The material consists of rod-shaped particles about 500A. long and 50–100A. across, with strongly crystalline *X*-ray patterns. This length corresponds fairly closely with the D.P. of the fraction, and it is therefore thought to consist of the crystalline regions of the fibre isolated from the more strongly degraded amorphous portions. M. L. Nelson and C. M. Conrad[46] criticize former determinations of crystalline/amorphous ratio based on determinations of first-stage acid hydrolysis, on the grounds that the insoluble residues contain insoluble polymerization products from the glucose produced during the degradation of amorphous cellulose. If this is first extracted with dilute caustic soda or ethanolamine, more reliable results are claimed. V. I. Sharkov and G. D. Paramonova with V. S. Muromomtsev[47] and with M. N. Klikasheva[48] have found that purified celluloses from sources as diverse as cotton and spruce have about the same proportions of readily hydrolysable cellulose (2·45–2·84%) and that the rate of hydrolysis of the crystalline residue is about the same in each case. Similar hydrolysis experiments were performed on the same celluloses after transformation into the corresponding polyuronic acids by the nitrogen tetroxide oxidation, and the hydrolysis rates were almost unchanged, showing that the hydrolysis is dependent far more on the arrangement of the cellulose molecules in the fibre than on the presence of non-cellulose material such as uronic acids. P. C. Mehta and

E. Pacsu[49] support Pacsu's 'ring structure' theory by further work. According to this theory adjacent chains of anhydroglucose units of the accepted 1 : 4-β-glucoside pattern are assumed to be cross-connected at intervals. Mehta and Pacsu consider experiments on rate of hydrolysis of the kind normally interpreted in terms of (i) rapid attack of amorphous cellulose and (ii) slow attack of crystalline cellulose. They claim that the first stage hydrolysis is too rapid to represent the breakdown of β-glucoside linkages and assume therefore that it represents an attack on the 'cross-linking' bonds. E. Husemann and M. Goecke[50] have also carried out work which suggest that different rates of degradation are due to the presence of bonds of different reactivity rather than to differences in accessibility. They oxidize cellulose in cuprammonium solution with gaseous oxygen and then note the end of the first rapid stage when an average D.P. of 400–500 is attained, i.e. much greater than that of Pacsu. This is taken to indicate that 400–500 unit 1 : 4-β-glucoside chains are connected with each other by bonds which are broken by oxidation in alkali, approximately 3000 times faster than the oxidation of normal 1 : 4-linked anhydroglucose units. T. Timell,[51] on the other hand, regards the periodate method of oxidation as very suitable for a determination of the crystalline/amorphous ratio, the cellulose first being transformed into the methyl ether.

There have been further attempts to elucidate the details of periodate oxidation of cellulose and other carbohydrates. G. Hughes and T. P. Nevell[52] have found the production of formic acid from glucose to continue for much longer periods than the time required for the reduction of the periodate. The p_H at which the reaction takes place is important and it is suggested that esterification occurs between the periodic acid and the carbohydrate as an intermediate stage. Comparable evidence is given by D. J. Bell, A. Palmer and A. T. Johns[53] who have also investigated the periodate oxidation of methylated monosaccharides at different p_H. In this case, inconsistent results, obtained in the presence of a phosphate buffer at p_H 7·5, are ascribed to complex formation between periodate and phosphate.

W. O. Kenyon and E. C. Yackel[54] have shown that it is possible to control the oxidation by nitrogen tetroxide of primary alcohol groups in cellulose to carboxyl so as to give a wide range of products of varying acid values and alkali solubility. This is effected by applying the reagent in carbon tetrachloride solutions of different concentrations, and W. W. Pigman, B. L. Browning, W. H. MacPherson, C. R. Calkins and R. L. Leaf[55] have produced the uronide of cellulose with mixtures of nitric and nitrous acids. F. S. H. Head,[56,57] who had previously had some controversy with Pacsu on the course of alkaline hydrolysis of periodate oxycelluloses, has adopted the following procedure : he has applied the periodate oxidation to a cellulose oxidized to the corresponding polyuronic acid with nitrogen tetroxide, oxidized the aldehyde groups formed at the 2- and 3-carbon atoms to carboxyl, and after hydrolysis has isolated *meso*-tartaric acid. This demonstrates by another route the validity of the now accepted transformation of the primary alcohol groups in cellulose to carboxyl.

Using accepted methods cellulose has been oxidized to give carboxyl

groups at the 6-carbon atom and the 2- and 3-carbon atoms. Z. A. Rogovin, M. M. Shorygina, A. G. Yashunskaya and M. G. Trevyas[58] have then esterified the modified products and have shown that the carboxyl groups have an important influence both on the course and rate of esterification and on the solubility and other properties of the product. The quantitative determination of the carboxyl content of modified and unmodified celluloses is an important criterion both of the extent of the chemical modification and also of the absorptive properties for anionic and cationic dyes. It has been effected by a variety of methods: absorption of a basic dye,[59] cation exchange in a modification of Neale's method, by direct titration[60,61] and combination with benzidine.[62] The back-titration of uncombined benzidine in the last method is effected by diazotization, coupling with R acid and colorimetric estimation of the dye thus formed. Two investigations have been made of the 'wet combustion' method for estimating cellulose by oxidation of the acid dichromate solutions.[63,64] The complexity of the reactions which occur has been emphasized and procedures to secure increased accuracy have been suggested.

The important special case of chemical modification by radiant energy has also been the subject of a few investigations. Most of the examples of this action considered at the Photochemistry Symposium of the Society of Dyers and Colourists were concerned with the behaviour of dyed textile materials and will be dealt with later. Two are of interest here. W. J. Whelan and S. Peat[65] have studied the analogous degradation of starch by ultra-violet light (unfiltered mercury arc) in the presence of oxygen, and, for some experiments, with zinc oxide as sensitizer. The results are of special value because they provide more detailed information about the photo-catalysed oxidation of a high-molecular carbohydrate than has been previously available. Terminal anhydroglucose units with the 1-C uncombined suffer breakage of the pyranose ring and oxidation to aldehyde at the 1-C and 3-C atoms, with the removal of the 2-C as formic acid. Groups in the chain undergo oxidation to aldehyde at the 2-C and 3-C as in a periodate oxidation, and terminal groups with the 4-C free are largely degraded to formaldehyde and formic acid. This stage is followed by a series of light-sensitized hydrolyses (producing D-erythrose and glyoxal) and further photo-oxidations leading ultimately to carbon dioxide.

H. J. Callow and J. B. Speakman,[66] in a study of the action of light on jute showed that, besides the more or less normal photo-degradation of the cellulose portion, the lignins, or oxidation-products of lignin remaining after an oxidative bleach, increase in colour during irradiation. This is ascribed to demethylation of the lignins and the possible ultimate formation of quinones. At any rate previous acetylation of bleached jute gives a product which goes lighter on irradiation.

H. F. Launer and W. K. Watson[67] show that depolymerization and modification of cellulose are retarded by water and unaffected by oxygen when the irradiating light is in the far ultra-violet, but are encouraged by these agents during near ultra-violet irradiation. It is considered that the short-wavelength radiation is capable of direct disruption of the bonds in the molecular chain, whereas the longer wavelengths are

capable of activation only. P. J. Flynn, J. E. Sands and K. S. Campbell[68] have studied some of the separate factors which contribute to the atmospheric tendering of cellulose. They state that a very significant part of the degradation can be ascribed to light action alone, and make the rather remarkable suggestion that the degradation produced by light from one portion of the spectrum can be diminished by simultaneous irradiation with light of other wave-lengths. Race,[69] who has also worked on this subject, concludes that during exposure in industrial atmospheres summer and winter are the periods of highest degradation. In summer oxidation is predominant and in winter, acid hydrolysis. A. Bollinger and N. T. Hinks[70] show an increased reducing power of cellulose exposed in the presence of tungstic, phospho-, boro- and silicotungstic acids. S. L. Perti, S. R. Ranganathan, T. S. Subramanian and L. R. Sud[71] have found that varying influences are exerted by various metal oxides applied to cellulose before exposure. Mn, Fe and Al inhibit depolymerization decreasingly in the order given; Cu, Sn and Ti accelerate it, and Cr has little influence.

T. Petitpas[72] has shown that when cellulose is heated in anhydrous glycerol up to 250° c. depolymerization occurs and is very pronounced at the highest temperature of treatment; it causes great loss in strength and extension at break. *X*-ray diffraction experiments showed that a new crystalline form of cellulose was produced.

An effect, which present information suggests is specific to the reagent, is described by H. B. Moore.[73] Cotton yarns which have been weakened by prolonged heating (160° c.) may have a high proportion of the original strength restored by treatment with dry liquid ammonia under pressure at 125° c.

Esterification and etherification of cellulose.—From a general point of view, and without emphasizing the origin or history of fibrous cellulose, the main development that has taken place during 1949 may be said to be the increase in the variety of new derivatives produced and described, and the associated modifications, which have been observed particularly, for example changes in the solubility in water, electrolyte solutions and non-aqueous solvents. These have in many cases great technical interest in fibre production, in finishing where completed yarns or fabrics are modified by reaction, or in finishing also, where the derivatives are treated in the same way as other plastics and applied in films of greater or less continuity.

On the other hand, the mechanism by which even well known cellulose derivatives are formed is by no means fully elucidated. In particular the influence of fibre structure and its partial or complete disorganization by the reaction mixture play a great part, not completely understood, in the final result. The most cogent evidence in this field comes largely from crystallographic data. Some notable contributions have been made in the period under review, both to the mechanism of formation and to the reverse mechanism of hydrolysis. In this survey, the properties and production of xanthates, the most important esters of cellulose for fibre production, will be reserved for the section on viscose rayon.

G. Jayme and U. Schenk[74] have proposed a test for the reactivity of native celluloses, and hence of suitability for esterification; this depends

on a standardized comparison of the degree of acetylation which follows a swelling pre-treatment with glacial acetic acid at room temperature with that obtained when swelling with the acid takes place at 90° C. N. Saito[75] has shown that the heat of acetylation of fibrous cellulose (from various sources) to the triacetate is fundamentally the same for all the forms and is largely independent of the acetylation conditions. E. Heuser, W. Shockley, A. Adams and E. A. Grunwald,[76] in choosing phosphoric acid as the reaction medium do so because of the low depolymerizing activity of the acid, but show that no water must be present initially if conversion to triacetate is to be complete when acetic anhydride is the esterifying agent. This medium allows acetic anhydride to be compared with glacial acetic acid as the essential esterifying agent, and it is shown that the latter is much less efficient even at high reaction temperatures (100° C.). Water-swollen cotton linters may be partially acetylated by keten[77] in ether solution with perchloric acid as catalyst. There is little degradation, but polymerization products of the keten are objectionable and have to be removed from the fibre. Reactions for progressing in both directions between tri- and lower acetylated forms have been patented by British Celanese Ltd.[78] The partial hydrolysis of the primary triacetyl cellulose is claimed to be accelerated by converting all the excess anhydride to acetic acid by addition of the necessary water, and then adding a neutralizing agent, which is intended to put the acid acetylation catalyst out of action. On the other hand, transition from a lower acetate to the triacetate is brought about by further treatment with the anhydride in an organic solvent, but without the use of a catalyst.

Cellulose propionates[79] and cellulose butyro-crotonates (up to practically complete esterification of the hydroxyl groups) have been prepared with reaction media containing the appropriate acids, their anhydrides and an acid catalyst; the methods adopted do not differ in principle from the normal industrial methods of acetylation. Esters which can be dyed with acid dyes are prepared from acetylcellulose by acyl group exchange with *N*-acyl-α-amino-acids.[81] An unusual procedure[82] in isolating the esters of higher aliphatic acids from their reaction mixtures is the removal of the accelerating acid (zinc chloride or hydrochloric acid) by a reagent which does not allow the acid to form ions, or presumably water, e.g. ethylene oxide or an olefine. It is claimed that the esters may then be precipitated in a perfectly clear form.

In the esterification of cellulose *via* the acyl chlorides (e.g. acetyl chloride), P. V. Popov[83] finds that the heterocyclic tertiary amines also present do not act as simple acid-binding agents, but as in other similar reactions through primary association of the chloride with the amine. This is supported by the marked change in rate and extent of acylation when pyridine is replaced by α- or γ-picoline. Cross-linking of cellulose esters by various bi-functional agents is of interest both theoretically and industrially. For instance, it is stated[84] that if secondary cellulose acetate is spun from acetone solution in the normal manner, with the addition of glyoxal or formaldehyde, and the fibre is then heated, cross-linking occurs at the free hydroxyl groups of the cellulose, and that this will persist, after the ester has been hydrolysed, to give a regenerated cellulose insoluble in cuprammonium. Treatment of a

secondary acetate with a number of inorganic halides, e.g. the trichlorides of As, Sb and P, phosphorus oxychloride and thionyl chloride, and subsequent washing to hydrolyse, gives a product in which the viscosity has increased and in which S, P, etc. may not be present.[85] The presence of aldehyde groups, produced by oxidation of cellulose at the 2 : 3-positions followed by acetylation, is shown to decrease markedly the solubility of the esters; this is ascribed also to cross-linking of the adjacent ester molecules.[86]

A phenomenon which may have a similar explanation is the increase in viscosity and final gelling of dilute solutions of cellulose nitrates in acetone solution after standing over a variety of solid basic substances.[87] The effect is increased if the carboxyl content of the ester is increased but is reversed by acids. Ultracentrifuge sedimentation experiments show that association of the cellulose nitrate chains is occurring.

Several studies have been made of the inter-relations of esterification mechanisms and the initial and intermediate structure of the material being esterified. F. Happey[88] has probably made the most complete and authoritative investigation. In considering the whole problem of esterification and saponification of both acetate and nitrate, a theory of conditional isomorphic interchange of the hydroxyl and the esterifying groups is proposed. That is, where the esterifying or accompanying acids do not readily penetrate the crystalline lattice of the cellulose, the interchange takes place primarily in the amorphous region and on the surfaces of the crystallites so that the lattice itself is not affected. This obtains especially in acetylation and the triacetate can be formed in the amorphous region leaving the lattice unchanged as native or hydrate cellulose according to the original lattice structure of the cellulose. The triacetate formed in this way can now be swollen by the acetylating acid and the crystallites are opened up leading ultimately to a fully acetylated material with a final hydrate-cellulose lattice if the swelling is sufficiently great. In intermediate stages it is possible also to de-acetylate without further swelling, so that the original lattice structure is not disturbed. This possibility of substitution, with triacetyl and unesterified cellulose in regions practically corresponding to the amorphous and crystalline regions respectively, is quite different from the state of affairs during nitration. Nitric acid can penetrate the crystallites and therefor progressive nitration with evidence of mixed di- and tri-nitrates takes place; a new lattice for trinitrocellulose is formed after a certain proportion of the total number of hydroxyl groups have reacted.

J. Chedin and A. Tribot[89] have studied nitration from the point of view of the reaction of hydroxyl groups with the nitrating acid. It is shown that although the phenomenon may be complicated by swelling and other effects of the water and sulphuric acid present, the degree of nitration depends primarily on the concentration of nitric acid. An observation which can well fit in with the detailed mechanism of Happey is that nitration is taking place in different parts of the fibre by different means, one through the diffusion of nitric acid in advance of the swelling agents, the other by the ternary mixture water–sulphuric acid–nitric acid.

T. Timell[90–94] has published a series of papers in which the etherification of cellulose with various groups and under a variety of conditions has been

exhaustively studied. The disposition of ether groups in partly methylated cellulose can lead to the simultaneous presence of all eight of the possible anhydroglucose units (e.g. one unsubstituted, three mono-substituted, three di-substituted and one tri-substituted). The distribution in many ethers prepared by methylation with methyl sulphate and alkali is similar to that which would be calculated from equal accessibility and reactivity of all three –OH groups and a random distribution of the methylating agent molecules. The 6-OH appears however to be more readily etherified than the 2-, and the 2- more readily than the 3-, and in mono- and di-derivatives the choice of the entering group is mainly between the 6- or the 2- and 3-positions. The reaction is more rapid on regenerated cellulose than on native cotton but other conditions and results are closely similar, and regenerated cellulose is more difficult to methylate uniformly. If the cupri-cellulose is methylated, complex formation between the copper and the hydroxyl in the 6-position appears to protect the latter from etherification. Alkali cellulose reacts with sodium β-chloroethylsulphonate to give a sulphoethyl ether of which the sodium salt is fully soluble over a wide range of substitution, e.g. as low as 2 sulphoethyl groups for 20 anhydroglucose units. The free acid is a strong one (with a dissociation constant equivalent to that of HCl) if the formation of carboxyl groups is avoided during its preparation.

C. W. Tasker and C. B. Purves[95] have extended the device of tosylation to an attempt to determine the position of the substituents in commercial hydroxyethyl celluloses; in this case esterification takes place on the primary alcohol groups of the substituent instead of exclusively on those of the cellulose. Evidence of substitution in the 2- and 3-positions has been obtained; and it is suggested that certain discrepancies arising during the prolonged esterification are shown to be caused by the attachment of polyethylene oxide chains furnished by previous polymerization of the etherifying agent. Other evidence of the positioning of etherifying groups and the influence of accessibility of different regions of the cellulose is furnished by T. Timell[96] in a study of the halogenation of tri-allyl celluloses. The absorption of halogen is in two stages, the first rapid, the second slow. These are considered to correspond to substitution, first in the amorphous portions of the tri-ether, then in the crystalline. The crystalline/amorphous ratio is shown to be very nearly the same as in the original alkali cellulose. In the production of carboxyalkyl ethers of cellulose,[97] the presence of higher alcohols in the etherifying mixture prevents undue swelling and dissolution of the resultant ether and renders its separation more effective. Carboxymethylation of cellulose in the form of yarn or cloth[98] was only partially successful in improving the resistance to permeability by water.

New methods of cross-linking cellulose ester molecules with polyamide intermediate chains have been suggested. In one,[99] polyamides of the 66-nylon type or the ω-caprolactam condensate type have been cross-linked with partially esterified or etherified cellulose through the free hydroxyl groups by the aid of formaldehyde or thiols. In another, cellulose is converted into an oxazolindone ether.[100] These can be xanthated and the alkali solutions used for making filaments by the viscose method. They can then be hydrolysed to the corresponding amino-ethers

which can be made insoluble through cross-linking with a dicarboxylic acid or ester (e.g. methyl adipate).

The reaction of cellulose with formaldehyde, of first importance in many anti-shrink finishes, has been studied in detail by J. J. Grundfest and D. D. Gagliardi.[101] The reaction is proceeding actively at 150° C. and the extent of combination is governed by the opposing factors of rate of reaction and rate of evaporation of the reagent. When the concentration of formaldehyde is low, the combining weight suggests the formation of simple methylene ethers; at higher concentrations it indicates that polymethylene links are formed.

The part played by the water in the industrial ethylation of cellulose is exploited and controlled as the result of detailed investigations by J. Cyrot, and J. Chédin and A. Tribot.[102] In the ethylation of alkali-soaked linters with neutral ethyl sulphate under reduced pressure there is shown to be an optimum pressure corresponding to each acylation temperature. Completely dry alkali cellulose does not react, but a partial vacuum removes water which would otherwise hydrolyse the ethyl sulphate. Water appears also to be necessary to produce a certain minimum swelling in the reacting cellulose, in order for the reaction to proceed.

Manufactured cellulose fibres

Viscose.—Much work still continues, with a considerable variety of experimental approach, on the complex relations of fibre structure and fibre properties, as well as the conditions of fibre production and treatment which give rise to these structures. On the side of industrial production, several new devices have been proposed for the continuous spinning and after-treatment of viscose, all of them representing changes in mechanical detail rather than in fundamental procedure. There are also a number of new suggestions for producing crimped, roughened or wool-like fibres, mostly with the object of increasing the fibre-to-fibre adhesion in spun staple yarns.

In the steeping process[103] it is recommended that the normal speed of introduction of lye into the press should be increased in order to obtain more uniform contact with the material before swelling can cause local exclusion.

S. N. Danilov, N. M. Grad and V. D. Klesman[104] have continued their detailed study of the xanthation reaction and now show that the thioanhydrides first formed by the interaction of carbon disulphide and soda cellulose are broken down by alkali solutions to form the sodium cellulose xanthate and free cellulose. The diethylacetamide derivatives of technical cellulose xanthates have been prepared and fractionation from aqueous ethylene chlorohydrin solutions has been carried out; this has shown[105] that both in the mode of substitution and in the chain lengths of the molecules a very considerable heterogeneity exists. This is ascribed, in part at least, to the slow penetration of the disulphide into the soda cellulose with consequent localized regions of intense substitution, and it is suggested that an improvement could be effected if a xanthating agent which is more soluble in caustic soda could be used. K. Lauer,

R. Jaks and L. Skark[106] state that xanthation affects mostly the 2-carbon atom in the amorphous region.

The structure and mechanical properties of cellulose xanthate sols and their mechanism of gelation either through self-decomposition or by the spinning bath is of primary importance. P. Herrent with G. Jnoff[107] and with F. Mouraux and A. Lude[108] have shown that important changes in ripening viscose, as shown by the viscosity under constant rate of shear, are closely paralleled by the titre of the same viscose with standard silver chloride. Both show a sharp change in value at the Hottenroth index which is taken to correspond to optimum spinning quality. The end-point of the titration is detected electrometrically.

Much attention has been paid to the problem set by difficulties in filtration of viscose solutions.[109] Clogging has been ascribed to highly 'swellable,' highly xanthated particles[110] and also to silica particles coming from the water rather than the pulp.[111] There is agreement that it is not due to unxanthated, undissolved cellulose more directly related to the range of molecular size in the original pulp. D. Vermaas and J. J. Hermans[112] first consider theoretically an ideal molecular network of a polymer-bearing ionogenic groups and then connect the swelling with external electrolyte concentration. From this an estimate of the molecular length of real gels can be deduced from their observed behaviour, and it is concluded that the molecular chain lengths in a xanthate network are not very long. An exhaustive discussion of the chemistry of the Lilienfeld strong-acid bath by P. Eckert and R. Wirén,[113] supported by a great deal of data, relates swelling of the filament at various stages to the poor properties of the resultant fibre; it supports in general the views of Lilienfeld himself.

Some aspects of the internal structure of cellulosic fibres have already been considered. There is, however, one feature which in its derivation is peculiar to some artificial extruded fibres and which has been specially defined and examined for viscose; this feature consists in the outer skin being very different from the fibre interior, as regards structural, mechanical, and optical properties. G. Landells, S. H. Mhatre and K. I. Narasimhan[114] have shown that this differentiation can be made more distinctly visible in the cross-section if a synthetic resin is first condensed in the fibre and this is followed by staining with a dye which dyes the resin. Normal zinc sulphate baths are thus shown to produce a well-defined skin, and ammonium sulphate baths a thin one. K. I. Narasimhan and J. M. Preston[115] have found that double refraction—a criterion of orientation—is higher for the skin than for the core. E. Elöd and H. G. Frölich[116] are able to remove this skin by superficial acetylation, dissolving away the acetylated portion with a suitable solvent. This enables them to demonstrate the properties of the core. The cores of viscose rayons spun into the acid bath appear then to have a more pronouncedly fibrillar structure than those spun by coagulating the viscose before decomposition. C. W. Hock,[117] in an examination of mechanically fibrillated rayons with the electron-microscope, shows that the fine structure of viscose fibrils is much less regular than that of the corresponding fibrils of cuprammonium.

In the field of production, a number of designs for thread-progressing

mechanisms for continuous spinning systems have been proposed.[118–124] The variations between them are almost entirely in mechanical detail and no new principle is included. The methods suggested for imparting crimp to viscose and other manufactured fibres are numerous and include: (i) slow coagulation followed by special tension cycles,[125] (ii) crêpe-twisting the wet yarn, drying and untwisting,[126] (iii) setting a false twist in a yarn impregnated with a resin pre-condensate, by heating followed by untwisting,[127,128] and (iv) spinning yarns in which some of the filaments have different shrinkage characteristics from the others, stretching beyond the elastic limit of the least extensible and relaxing.[129] An importation of the cold-drawing technique from the synthetic fibres to viscose, in order to produce high-tenacity filaments consists in producing filaments with a minimum of applied tension and fully relaxed before regeneration.[130] Such filaments show the 'necking-in' properties, characteristic of nylon, on drawing.

Two books of special value in the provision of technical information on viscose staple fibre, are 'Fibro,'[131] edited by C. M. Whittaker, and dealing principally with spinning preparation, weaving and processing, and FIAT Report 937, by O. v. Kohorn and J. L. Costa,[132] dealing principally with production machinery for the fibre.

Cellulose acetate fibres.—No very important innovation has appeared in this field. A wet-spinning process for acetates of low acetyl content[133] (40–45%) claims, as is to be expected, that a rayon of enhanced softening temperature is produced. The acetate in an aqueous–organic solvent mixture is spun into an aqueous bath containing ammonium acetate. A fibre of more homogenous structure is claimed to be formed if the extruded acetate solution is heated by a high-frequency alternating electric field while surrounded by an atmosphere rich in the solvent vapour.[134]

Studies of various aspects of saponification have been reported. A method for producing regenerated cellulose yarns from highly stretched yarns of acetate is as follows: the tension of the yarn in its passage through the hydrolysing solution is maintained constant by varying the rate of travel through the different parts of the bath, in order to compensate for the dimensional changes produced at the corresponding stages of the saponification.[135] In another process, stretching of the acetate is accomplished in steam and is facilitated by the presence of a plasticizer which is gradually hydrolysed by the steam so that its effect is only temporary.[136] C. P. Tattersfield[137] has shown that the rate of saponification of acetate rayon is much accelerated by various forms of mechanical strain, the original rate of saponification being restored by treatment in hot water or in hot salt solutions. S. Simmens and F. Howlett[138] have given a detailed description of what must be the causative factor for this effect. When they are stressed cellulose acetate filaments or film develop minute internal cracks, both superficially and internally. The pattern of these depends on the condition of the material when the strain is produced.

Alginate rayons.—To keep solid impurities fully dispersed in alkaline alginate spinning solutions a cation-active agent has been added to the bath,[139] and the production of insoluble alginate filaments by a continuous spinning process has been patented.[140] There has been some

controversy on the reason for the contraction, followed by swelling, which occurs when water-swollen alginate rayon is placed in salt solution. H. G. Ingersoll and A. A. Johnson[141] believe the first effect is due to loss of water by osmotic action, reversed as the salt molecules diffuse into the fibre. I. MacArthur, J. L. Mongar and A. Wassermann[142] reiterate their previous statement that it is due to breaking of calcium cross-links by ion-exchange. Cross-linking of alginate molecules to prevent the disrupting effect of base exchange in alkaline baths has been effected with diepoxy-compounds, e.g. hexylene-1 : 2, 5 : 6-dioxide.[143]

Preparatory processes

Sizing and desizing

As already noted there has been much activity in investigations concerned with the constitutional and colloid chemistry of starches and related carbohydrates. This is significant both for sizing and for printing operations but as the most critical demands are generally made by the printer, these developments will be discussed in the section devoted to printing.

On the other hand whereas desizing, especially by enzymic decomposition also interests the printer and finisher, it is of greatest interest in the preliminary cleansing of fabrics and will therefore be discussed here. There have been few suggestions which might lead to any radical modification to the processes of cotton warp sizing either in machinery, materials or procedures, but the new synthetic fibres, cellulosic and non-cellulosic, still present problems which have not yet been satisfactorily solved, and therefore some attention is given to processes which affect wholly or partly the non-cellulosic manufactured fibres.

In the general investigation of sizing efficiency contributions have been made by E. Bradbury[144] and also by E. Bradbury and H. Hacking.[145] These consist of reduced-scale sizing experiments upon warps which are woven under standard conditions, giving data such as end-breakage distribution and frequency, specified cloth faults, etc.; they are analysed statistically to give values reflecting the efficiency of the size and its conditions of application. To assist in this work a test has been devised in which filaments are cut deliberately at the back-rest of the loom so that the adhesive action of the size during actual weaving may be assessed. These methods of investigation are sound as they represent a testing of the sized yarn—under controlled conditions of actual usage. The number of variables that enter into the behaviour of sizes and yarns in sizing, preparation and weaving is large; experiments of this kind are therefore laborious and results in variety are likely to be slow in accumulating. The impression is gained that these workers could progress more rapidly if their experiments were supported by a more complete initial selection of sizing materials etc. on the basis of chemical and physical tests. Among many practical discussions in trade periodicals of the techniques of sizing, a useful wide-range discussion is given by a conference of Textile Operating Executives of Georgia[146] and in a long series of articles with extensive bibliography by P. V. Seydel.[147]

A suggestion for increasing the strength of grey cotton yarn[148] which perhaps borrows from the technique of mercerization under tension consists of swelling cotton to a limited extent by hot alcohol–water mixtures and drying under tension. The normal method of adjusting size properties by varying the composition in respect of the variety and proportion of the adhesives has been extended to use newer materials, the quick-gelling and soft-film forming properties of farina being modified by the addition of starches high in amylopectin content (e.g. waxy maize).[149] The introduction by Monsanto of silica gel dispersions for conferring anti-slip properties on yarns is by now well established. The same firm[150] now claim that silica-sol solutions when applied to the yarn and dried confer greatly increased yarn strength. Dispersed wax lubricants with a specified polyoxymethylene–fatty acid condensate as dispersing agent are said to be readily removed in the scour.[151] Other interesting proposals are (i) for acetate rayon–casein dispersed in an organic alkali solution plasticized with triethyl phosphate[152]; (ii) for nylon–acid casein dispersed with an agent of the sulphonated formaldehyde–phenol condensate type, with a free fatty acid as lubricant to assist removal[153]; (iii) an alkyd resin also modified with a fatty acid[154]; (iv) for Terylene–polyvinyl alcohol–acetate with boric acid or barium chloride, formaldehyde–alkylolurea, casein, rosin or an alkyd resin.[155]

R. Haller[156] has attempted a definition of soluble starch as falling within a precise range of moderate degradation. Thus while the Fehling number should be low and the full blue iodine colour should be preserved, the starch should be capable of reducing flavanthrone in alkaline solution.

The mechanism of enzymic degradation and synthesis of starch has been continued by N. Haworth, S. Peat and others.[157–159] This amplifies and greatly modifies previous theories based on the action of so-called sensitizing enzymes. These enzymes are assumed to transform dextrins by break-down and re-synthesis into products which can be more readily attacked by the principal enzyme; this makes it necessary to reconsider the structures that have been proposed for the 'branched' starches (e.g. amylopectose). R. B. Alfin and M. L. Caldwell[160] have obtained results in studies of the action of pancreatic amylases on starch fractions. These results suggest that a compensatory mechanism functions, and that the primary reducing dextrins are formed more easily from branched than straight-chain fractions; however those formed from branched fractions are further hydrolysed more slowly. The advantageous effect of common salt on desizing preparations rich in α-amylase is well known. V. L. Erlich and G. M. Burkert[161] have further studied the effect of a variety of salt additions to water used for extracting barley; they have shown that these both increase the yield of α-amylase and enhance its amylolytic effect. Two reports have been made, from different sources, of powerful dextrinizing and saccharifying enzymes produced during the culture of common micro-fungi, e.g. *Aspergillus niger*.[162,163]

The claim has been made that treatment with alkaline hypochlorite solutions, followed by a short run in boiling soap, will remove starch sizes from viscose.[164] This would seem to need critical examination before acceptance, since other experience has shown that starches modified by hypochlorite treatment are often very difficult to remove from the fibre.

Scouring, cleansing and bleaching

On the general subject of cleansing, as distinct from scouring and bleaching of textiles for the purpose of producing a white finish or preparing for the application of dyes, there have been a few innovations, mostly in detail rather than in principle. Much greater interest is being shown in ion-exchange media for the purification of process waters and they are proving to be extremely powerful means for the selective removal of unwanted ions. The range of these agents already well established (the insoluble natural and artificial zeolites and the cation-sequestrating polyphosphates) is likely to be increased. The synthesis of numerous surface-active agents still goes on, and the development of this trend—which affects other important industries besides those concerned with textile processing—would require a separate report. On the whole, more attention has been paid to the cationic agents of special application and to the non-ionogenic than the anion-active ones. The specific use of soluble cellulose ethers as stabilizing and dispersing assistants to detergent solutions continues in popularity and new variants are being suggested. In scouring of piece goods—especially cotton in the open width—further information about the continuous alkali–pad–steam processes continues to be given and improvements continue to be suggested, mostly in the details of plant construction. Further extensions to the use of fluorescent substantive compounds ('optical bleaching agents') especially in the field of domestic detergent preparations are still being made, and new fluorescent agents still proposed. The kinetics of the decomposition of alkali-metal hypochlorite solutions have for many years received detailed study. These studies are being continued, with special emphasis on the interaction between hypochlorites and chlorites.

An authoritative summary of the subject of ion-exchange resins has been given by C. W. Davies[165]; J. D. Guthrie and others[166,167] have made ingenious use of phosphorylated and amidized cotton—shown to be efficient cation- and anion-exchange agents respectively—by obtaining the treated cotton in the form of fabrics; these fabrics have much more advantageous mechanical properties than the loose fibre. Precipitated lime and magnesium salts are settled more rapidly during softening if aluminium alginate[168] is simultaneously precipitated or if addition is first made of a stable particulate suspension of insoluble alkali metal carbonate, on which the precipitated hardness can collect.[169] The action of soluble cation-sequestrating polyphosphates can be advantageously controlled as follows: the possibility of an ion-interchange apart from that of the dissolved ions of the natural water[170] is introduced; the added metal ions are different from those (generally Na) initially present in the polyphosphate.

In assessing the hardness of waters by titration with standard soap solutions, the suggestion is made that the alkalinity introduced by excess soap solution and detected with phenolphthalein is a more sensitive indication of the end-point than lather formation.[171] P. Anglaret[172] has studied the reaction between sodium carbonate and calcium oleate in boiling suspension over several hours and has shown that only in the presence of a large excess of the soluble carbonate is an appreciable proportion of curd reconverted to sodium soap.

Two methods have been suggested for the estimation of ionogenic synthetic detergents in commercial preparations or in solution: sulphonic acid derivatives are precipitated with benzidine and back-titrated with standard alkali[173] and either anionic or cationic agents are titrated with standard solutions of dyes, which possess coloured ions of opposite sign, in the presence of some non-miscible solvent for the dye-agent complex.[174]

J. W. MacBain[175–178] has, by a variety of experimental methods, added to the long series of studies on the structure of soap solutions already published. In this field too G. S. Hartley[179] has shown how his theory of spherical aggregate distribution can be reconciled with *X*-ray diffraction pictures which have been taken by MacBain and others to indicate a lamellar disposition of soap molecules within the solution.

Extremely interesting results are obtained by J. Hypia[180] with an apparatus which records photographically the spread of surface-active solutions on different kinds of surface. This method enables not only the initial action of spreading to be shown, but also the effect of adsorption at the interface upon the continued spreading of the solution. The study of the adsorption of surface-active agents upon wetted surfaces, after synthesizing agents containing radioactive tracer elements[181] suggests that similar methods of investigation may be very useful in studying the absorption of dyes, finishing agents etc.

Carboxymethyl cellulose has been investigated in detail by various workers[182–187] and the results agree generally in principle, though there is some difference of opinion in detail. As a soil-suspending auxiliary to fairly concentrated pure soap solutions it does not appear to confer any marked advantage. With solutions of reduced soap content assisted by phosphate or silicate builders or with synthetic detergents it gives improved performance. It stands high among colloidal suspending agents used in the same way, and its absorption on the fibre can give rise to a lubricant action which protects the goods being processed from abrasion.

Retting represents a special kind of preparative cleansing treatment for textile fibres of the bast variety and can therefore be included here. An account has been given of the aeration method of flax retting developed in this country during the war.[188–189] The retting bacteria are largely anaerobes which can still live and multiply within the flax stems when the retting liquid is aerated.

Aeration however encourages the aerobic fermentation to gases of the removed encrustants and therefore greatly diminishes the difficulties of effluent disposal. On the other hand the retting of ramie[190] appears to be best accomplished by common aerobic bacteria, the efficiency of which can be enhanced by the removal of tannin and the provision of extra nitrogenous compounds. Sodium chlorite has been suggested as a chemical degumming agent followed by a caustic scald[191]; P. B. Sakar and H. Chatterjee,[192] on the other hand, do not find very favourable bleaching action with this reagent in the presence of natural encrustants. The same workers with C. R. Nodder[193] find that calcium-precipitating ions encourage the retting of jute.

The increased removal of impurities from raw cotton after it has been treated with dilute acid, either by aqueous or by organic extractants, was

first recorded by Knecht. This observation has been confirmed[194] and adduced as a justification for the grey sour as a preliminary to scouring.[195]

The Mathieson scour (alkali–pad–steam) has been supplemented either by a pre-treatment with cold dilute alkali and standing, or a longer interval between alkali-padding and steaming. This confirms the importance, noted by other workers, of the presence of an adequate proportion of alkali in the cloth before steaming starts.[196–198] The plant for steaming has been improved to increase the content of cloth in the steamer by devices which fold it in pleats on conveying lattices.[199] In a scouring steamer of Proctor and Schwartz Incorporated[200] the scouring liquor is sprayed through steam injectors along with steam on to the cloth during its passage.

Few really new suggestions have been made for the use of oxidative bleaching agents. The use of air or gaseous oxygen in cloth impregnated with hot alkaline solutions, mostly by injection of the gas into the circulating system of a kier, has been proposed from time to time, but has never found general favour. I.C.I. Ltd.[201] now adopt this principle in a new form for the bleaching of cloths containing vat-coloured effects where careful regulation of the severity both of scour and bleach is essential. In this method a cloth is impregnated with caustic soda and steamed, the scouring action being accompanied by the bleaching action of a regulated amount of air. It has been suggested that the powerful bleaching action of hypobromites at 7·0–8·2 p_H should be exploited for bleaching processes where hypochlorites are now used.[202–206] It is true that the maximum oxidizing action of hypobromite occurs at a lower p_H than that of hypochlorite; but it is likely that most careful control will be necessary to avoid cloth damage. The statement by W. Kind[203] that a danger-zone occurs at p_H 7 and below in bleaching cellulosic materials with stabilized peroxide solutions is interesting and surprising, as normally the oxidative effect of dilute peroxide solutions is at a maximum at much higher p_H values.

Some attention still continues to be paid to the conditions of application of chlorite and hypochlorite–chlorite bleaching reagents. It is frequently suggested that chlorite in such reagents is the principal oxidizing agent, its decomposition being accelerated by hypochlorite. M. Kozlov[204] however suggests that this mechanism is incorrect. He finds that the hypochlorite gives up its oxygen more rapidly in the presence of chlorite whereas the chlorite itself decomposes only slowly. Chlorine–chlorine dioxide solutions have been proposed[205] as effective bleaching agents with a low tendering risk, and continuous bleaching has been carried out by impregnation with hypochlorite–chlorite solutions (ratio av. chlorine 1·5/1 ; total av. chlorine 2·5 g./l.), steaming and piling, hot for 1 hr.[206] It has been shown[207] that very few surface-active agents, such as Tergitol O8 and Gardinol LS, are efficient in assisting the penetration of bleaching powder solutions into cloths. W. J. Atkins and H. J. Callow[208] have found that the colour which develops in bleached jute presumably from the changes in the oxidation products of the original fibres may be avoided by applying an acetylation mixture after the bleaching, with hypochlorite or peroxide. The oxidation of cellulose with dinitrogen tetroxide to produce a polyglycuronic acid has been exploited

industrially[209] for the production of absorbable dressings by the treatment of surgical cotton gauzes with this reagent.

Dyeing

From the practical point of view, processing developments have been dominated by the continuous methods for handling open-width fabrics. The general outlines of procedure have already been worked out, especially for the vat dyes applied in low-affinity forms (e.g. the Dupont pad–steam method) and also for procedure as influenced by special forms of impregnating, developing and steaming units. Now work is continuing on the selection of suitable dyes, on the adjustments necessitated by different cloth structures etc. One important factor is the effect of high temperatures upon the dyes themselves both through their influence upon the kinetics of dyeing and their influence on the stability of the dyes themselves. G. L. Royer, C. L. Zimmerman, H. J. Walter and R. D. Robinson[210] have studied dyeing action of a number of different classes of dyes with a variety of textile fibres at temperatures between 200° and 300° F. The most spectacular results have been obtained with those dyes and with those fibres where penetration is normally low at ordinary dyeing temperatures, and with some of these combinations the rate of diffusion has been increased many times. The high temperature has been shown to accelerate the decomposition of many dyes to a serious extent, especially through reduction by the fibre substance, but practicable methods of application by padding followed by high-temperature steaming have been worked out. The subject has also been studied by the Piedmont and Philadelphia sections of the American Association of Textile Chemists[211] and Colorists. These investigations, in general, parallel those which have just been cited, and valuable increases in speed of absorption, levelling and penetration have been noted, though the penetration effects are not always as marked as those described by Royer *et al.* Special attention has been given to the stability of the reduced forms of vat dyes, and the unique protective properties of so-called alkali–labile dextrins (probably starch degradation products with high carboxyl values) has been noted. Another important factor in the successful operation of continuous dyeing processes is an accurate and detailed control of the padding stage. A number of the variables of this stage have been investigated by G. L. Royer and C. L. Zimmerman[212]; such factors include speed of passage, time of immersion, temperature, cloth and yarn construction, the presence of wetting agents, etc. The results are generally in conformity with experience, but one most interesting discovery is that, according to conditions, preferential absorption either of water or of dye by the cloth from the liquor may occur in the box and at the nip. The Williams-box unit has been improved[213] by arranging the height of each successive well so that the forward displacement of the liquor by the cloth moving rapidly in the narrow channel may be balanced by the greater lift required in passing from one channel to another. This confers the benefit of mechanical penetration caused by the resistance of the liquid to movement, without too great a carry-forward. Although not strictly within the purview of this report the account of continuous dyeing of wool in multi-box machines by R. Casty and E. Krähenbühl[214] must be

mentioned, for it also introduces the principle of maintaining from the first a predetermined partition ratio of dye between the cloth and the liquors through which it is passing.

Of greater interest too, to both dyer and printer are the developments of a process, suggested many years ago in England and extended in Germany, and then in this country, the U.S.A. and U.S.S.R.[215] This is the use of heated fusible metal baths through which the cloth is passed in direct contact with the metal. This process has uses in the continuous application of dyes to cloth, their fixation, development of prints, fixation of resin precondensates, drying of moist cloth, etc. In a process developed by Mortons Sundour Fabrics, R. S. E. Hannay and W. Kilby,[216] dye liquors and other aqueous solutions for treatment may be floated on the top of the metal bath.* One of the incidental advantages claimed for metal baths, especially if they are made deep, is that a useful regular pressure is exercised on the fabric as it passes through them. New steamer designs are being proposed, one in which simultaneous provision is made to subject the cloth to the alternate action of steam, and cooled treating liquors[217]; in the other, the saturated steam impinges on the cloth at high velocity through a series of jets.[218]

More data are now available for the critical assessment of the value of hooded dyeing machines. D. K. Ashpole, R. A. MacFarlane and C. C. Wilcock,[219] have given an account of a careful examination under works conditions of the improvement in steam-consumption, rate of dyeing, penetration, uniformity of dyeing temperatures, and freedom from soiling which results from enclosing winch dyeing machines. The higher operating temperatures in conjunction with the use of softened waters cause reduction of some direct dyes on regenerated cellulose fibres, and an adjustment of the dye-bath p_H may be required to combat this effect. It has been emphasized that the enclosure of jiggers[220] has an even more important advantage, since most of the dyeing in this machine takes place outside the bulk of the liquor. By protecting the batches from rapid and irregular cooling, more uniform dyeings can be produced with greater speed.

In the field of general dyehouse organization, as well as control of the quality of the goods produced by systematic testing against carefully designed standards, two papers have been given by R. A. MacFarlane and C. C. Wilcock, the first[221] on the special problems of preparing, dyeing and finishing rayon staple fibre materials, the second[222] on measures for the maintenance of appropriate quality in the processed article. It is a most comprehensive treatment, and forms a useful epitome of tests which may be applied in the control of production.

The Society of Dyers and Colourists' classification of direct cotton dyes is based on extremely simple tests and there have been a number of criticisms which suggest that discrimination is therefore not as accurate as it might be. It is also sometimes claimed that the actual conditions of testing may form an erroneous model for the large-scale application of the dyes. For instance, W. Armfield[223] has carried out rate-of-dyeing

* Since this account was written, further details of this process have been published. The indications are that it will cause a revolution in the application of vat dyes, and in piece-dyeing generally.

experiments in which salt is added at a constant rate throughout the dyeing operation. A few dyes, under these conditions approach the ideal behaviour of constant rate of exhaustion, but in most cases, deviations according to a restricted number of patterns take place. For non-levelling dyes, this work shows that compatibility may be assessed more accurately on the basis of this form of determination than on standard half-dyeing times measured with a single salt addition. J. A. Woodruff[224] has suggested some modifications of the S.D.C. classification to obtain results more fully applicable to viscose package dyeing. A direct measurement of diffusion rates into solid regenerated cellulose blocks is used as an investigatory technique.

Apart from the interest in pad–steam methods, little new about the vat dyes has been reported. The use of a hydrosulphite bath of lower p_H than the ordinary caustic soda baths (i.e. after vatting in caustic hydrosulphite, and buffering the vat with sodium carbonate) has been suggested by Du Pont,[225,226] and has been applied in various dyeing and fixation processes. The phenomenon of difficultly reversible change in vat dyes, particularly in the indanthrone group, on reduction and re-oxidation, has often been ascribed to 'over-oxidation,' but J. Müller[227] now brings forward evidence to suggest that it may very frequently be due to a change of the normal quinol leuco-compound into a more stable keto form (oxanthrone). This is favoured by a range of alkali concentrations, or high hydrosulphite concentration and is found even in vat-acid preparations. Besides the indanthrone group it is noted in simpler anthrimides, some carbazole derivatives, pyranthrone, etc. and is a notable cause of poor colour yields. M. R. Fox[228] has given an extensive and most useful summary of the constitutional chemistry of the vat range, with the object of showing consistant relations between the molecular constitution and various dyeing and fastness properties. The late A. Geake[229] has investigated, on classical quantitative lines, the absorption and desorption of two vat dyes, Caledon Jane Green and Caledon Red BN on cotton yarn. The experimental difficulties of this work are much more onerous than in corresponding work with direct dyes, especially in the control of the accompanying electrolyte concentration, in purification of the dye, and in the maintenance of the dye in its fully reduced form. Both dyes are shown to exhaust very rapidly in the initial stages and to reach an equilibrium absorption. With one or two discrepancies which are shown to be connected with the state of reduction, desorption is practically the inverse of adsorption. By comparison of absorptiometric with potentiometric measurements it is shown that complex formation with pyridine is probable, and that this is related to the lower absorption observed in presence of this substance.

H. A. Standing and J. O. Warwicker[230] have continued their research into the absorption of Chrysophenine G. They have shown that in specially prepared regenerated cellulose, changes in the equilibium absorption with varying p_H value and with varying liquor/cellulose ratios are due to the carboxyl ion content of the cellulose. Another quantitative study of a dyeing process,[231] not immediately relevant to this section but of great interest nevertheless, is a study of the mechanism of chrome dyeing processes on nylon ; special attention is given to dichromate ion

absorption, dye absorption, reduction of dichromate ions on the fibre and formation of chrome–dyestuff complexes.

Work continues on the dyeing of cellulose acetate fibres in the presence of carriers (adjuvants to the dye-bath, or used in pre-treatments, which possess limited swelling action for the fibre, and greater or less solvent power for the dyes).[232] The general tendency has been to extend the range of dyestuff classes to which this technique can apply. The technique has included the continued use of dispersed acetate dyes in the presence of carriers.[233] It has also included : (i) the application of vats and insoluble azo-colours[234] ; these are pre-treated in a solution of ammonium thiocyanate with the addition of an organic swelling agent, aniline black, and other oxidation colours (with a similar carrier system)[235] ; and (ii) acid dyes by a padding method with addition of ethyl alcohol and sodium thiocyanate.[236]

The success of the temporarily solubilized form of a blue phthalocyanine dye (Alcian Blue 8G)[237] has led to the suggestion for other solubilizing groups (e.g. ternary sulphonium, *iso*thiouronium,[238] and sulphonamide[239]), and the principal of solubilization by comparatively loosely attached basic groups has now been extended to insoluble anthraquinone colouring matters.[240] It may well be that this system of applying otherwise insoluble colouring matters can be very widely extended in the near future, and a new dye application class will be evolved. Considerable modifications in shade can be obtained when amino-phthalocyanine dyes are diazotized and coupled with selected components on the fibre.[241] Here also there seems a prospect of further important extensions of the phthalocyanine structure into the field of dyeing and printing. While on the subject of dyes which are essentially in the pigment or lake form after application to the fibre, attention should be drawn to the important work of F. A. Hamm and E. V. Norman.[242] They have shown that both copper phthalocyanine and indanthrone are capable of existence as crystals in different polymorphic forms and possessing different colours. This may perhaps be extended to other dyes, and the 'particle-size' theories for explaining the changes in hue of dyeings on soaping etc., may need much amplification.

A good deal of discussion has taken place on the constitutions, properties, and methods of use of the fluorescent 'white dyes' or 'optical bleaching agents'[243–246] but little fundamental innovation has taken place. There has also been an extension in the ranges of dyes ; mostly directs, suitable for copper after-treatments or containing copper in the molecule.

Space does not allow a detailed account of the many important contributions, both fundamental and practical, to the Photochemistry Symposium of the Society of Dyers and Colourists[2] and these transactions are readily available either in that Society's journal or in a separate volume. Attention should also be given in this field to the technique of H. Lanigan[247] which enables the tendering action of active vat dyes on cellulose to be related to the wave-length of the incident light. Other interesting work has been done by G. S. Egerton.[248] He gives evidence that tendering of active vat dyeings on cellulose, cellulose acetate, silk and nylon by the simultaneous action of light, water and air is attributable to an intermediate formation of hydrogen peroxide.

Textile printing

The main progress in this branch, as far as the industrial operation is concerned, has been : first, the further improvements of screen printing appliances, largely in the direction of mechanizing the operations of printing-down and drying ; secondly, suggestions for improved media in the revived technique of pigment printing ; thirdly, secondary modifications in roller-printing machines, and improved steaming equipment. There has also been some progress in the development of new thickening agents with the object of improving the mechanical properties of printing pastes and of securing ease of preparation, stability and improved colour yields.

There are also welcome signs of more fundamental enquiry into one or other aspects of printing techniques, processes and styles. Some mention has already been made of investigations into the constitutional properties of starches, gums and other high-molecular carbohydrates of special interest as printing thickeners. The relative proportions of unbranched and branched-chain constituents in natural starches and the effect of hydrolytic and oxidative reactions in pre-treatments are of vital interest for two reasons. They determine the important physico-mechanical properties of the paste and thence its behaviour during the making of the impression by roller-machine or screen. They may also be found to influence profoundly the processes of dye transfer from the impressed paste to the underlying fibre substance. Many contributions have been made to the details of amylose–amylopectin fractionation techniques[249–262]; these include improvements of the butanol method, with thymol and *cyclo*hexanol and with aluminium hydroxide, investigations based on iodine titration methods and end-group determinations by periodate oxidation methods. Other work extends present knowledge on the stability of starch gels including retrogradation processes. The stage seems to be set for an extensive isolation of amylose and amylopectin and a study of the properties of pastes in which these components are mixed in predetermined proportion. R. H. Munshi and H. A. Turner[263] have started a study into the mechanisms of dye-transfer between the thickener and fibre phases of a print during steaming ; the phases consist, for simplicity, of a film of thickener substance and of fibre substance (starch and cellulose respectively). The high concentrations of direct dyes in the phase external to the fibre, as compared with normal concentrations used in dyeing, are shown to have a marked influence on the extent of exhaustion but little on the rate. The electrical boundary conditions at the interphase seem to be markedly different from those set up during dyeing, and the favourable influence of anionic groups in the thickener, e.g. with sodium alginate or starch carboxyethers, is clearly demonstrated. Further unpublished work with dyes of low substantivity (e.g. acid dyes and indigosols) indicates that the distribution of dye in the two phases may be dependent upon the moment-to-moment distribution of water therein. A somewhat similar qualitative investigation by microscopic examination of prints at various stages of their production has been made by R. Haller.[264]

A great deal yet remains to be learned of the conditions within the steamer and their influence upon the final print, especially with respect

to the capacity of the steam to take up or to give water to the cloth passing through, as also to the simultaneous influence of temperature and water content upon the reactions steaming is intended to promote. Investigations by F. Fahnoe[265] with a pilot steamer fitted with a full complement of measuring instruments are of special interest. The A.A.T.C.C., Rhode Island Section[266] have again taken up the question of colour yield with vat dyes as influenced by steaming conditions, and the necessity for adequate temperatures in dealing with difficulty-reducible dyes was again stressed. There needs also to be an adequate amount of moisture in the system. Other work of special interest with this dyestuff-class is that of T. I. Kunin[267] on the heat-decomposition of sodium formaldehyde sulphoxylate. The inter relations of temperature with initial and final p_H are complex. Low temperatures in general lead to preferential decomposition of the sulphoxylate and a rise in p_H, whereas high temperatures lead to the formation of formic acid from the formaldehyde and a fall in p_H. A novel localized effect is described by C. P. Tattersfield[137] and may have some influence on the printing of acetate rayon fabrics. Strains of various kinds, including localized strains produced by embossing, greatly increase the rate of saponification of acetate rayon, so that cross-dyeing is then possible to give two colour effects.

Pigment methods are still being described. Various devices are suggested for obtaining a medium of good printing qualities, lack of distinctive colour, and capacity for transformation into a stable adherent film without marked stiffening of the printed fabric. Most of the pastes as applied are water-containing emulsions. The chief film-forming constituents cover a wide range; examples are di-*n*-butylmethylolurea and ethyl cellulose,[268] ether derivatives of melamine–formaldehyde condensates,[269] tristearin-tris-(carbato-methylpyridinium)-trichloride,[270] casein–formaldehyde subjected to metal after-treatments,[271] vinyl acetate–allylidine polymers,[272] vulcanized oils–casein–urea–formaldehyde mixed condensates,[273] *N*-methoxymethylpolyhexamethylene adipamide,[274] polyvinyl–urea–melamide resins,[275] and metallic (Cr) alginates.[276]

There have been some elaborations of the method by which salts of simple aromatic sulphonic acids are added to indigosol printing pastes with specified thickeners in order to improve colour yield. Various naphthol sulphonates have been suggested,[277–278], as well as naphthol-methane-ω-sulphonic acids in which presumably the acid group is detached on steaming. On the other hand, the uptake of indigosols when they are comparatively insoluble is improved by dispersing them with salts of complex aliphatic bases.[279] Self-development of stabilized azo-combinations during steaming is claimed to be improved by using acid-generating esters, e.g. diethyl tartrate, instead of the more usual acid-generating salts. It is possible that the solvent action of some of the suggested esters has a beneficial effect.[280]

In view of the increasing importance of the coppered and copper-containing direct dyes as ground colours for some dress styles, efforts are being made to improve the range as a whole by increasing the discharge-ability of those dyes, which do not readily give a pure white discharge. One of the most interesting of the suggestions that have been made is that of including an agent in the paste which will liberate cyanide ions.[281]

Another type of co-ordinating agent for the liberated metal atoms is ammonia or amines used in solution to wash the discharged print.[282] The device of whitening-up discharges by incorporation of pigment material in the print-paste is well known. It is now suggested that the pigment should be fastened more firmly by incorporation of a synthetic resin.[283] An alternative method for whitening the discharge, though not for delustring it, is by the presence of one of the new fluorescent 'dyes.'

The importance of 'carriers,' i.e. substances which may be considered as swelling the fibre substance with simultaneous improvement in the dispersion of the dye, has already been considered, but it also plays a very important part in suggestions for improved printing methods on rayons generally and for non-cellulosic synthetic rayons in particular. This extends from the use of urea in the dyeing of acid dyes on viscose,[284] caprolactam and thiourea[285] for printing on cellulose acetate with the same classes, ethanol for anthraquinonoid acetate dyes and diethylene glycol for vat dyes on Terylene[286] etc. The highly specific and uniform content of primary amine groups in nylon allows a new combination of the principles of reserve and discharge printing.[287] The reason is that a nylon fabric dyed with an acid dye is printed with sulphuric or other esters of complex hydroxy-amines, which when steaming takes place, liberate sufficient acid to displace the dye itself; the residue presumably combines with and solubilizes the ejected dye.

In printing machinery, improvements have been proposed in the construction of screen frames.[288] Innovations also include a machine which operates the squeegee at a uniform contact pressure, independent of the worker,[289] pasting-down machines, drying machines and picking-up reel, all working along the table. A completely automatic screen printing machine, has also been developed.[290–291]

It is a matter for speculation why so many roller-printing machines are still provided with hand-operated box-wheels for registration while the corresponding machines for high-speed photogravure work on paper have elaborate and instantaneously-acting devices which do not necessitate slowing down the machine while adjustments are being made. Automatic devices are suggested from time to time, but rarely seem to be taken up. One such device, recently suggested, seems to be mechanically sound.[292] It is also interesting to see that hydraulic loading, long practised in calenders, should now be suggested for the nips of roller printing machines.[293] One interesting development in paper printing which may extend to textile printing, though some modifications would be required, is the use of a high-voltage electric field to transfer the colour from the printing roller to the article being printed without direct contact between the two.[294,295]

Finishing

The literature which deals with this widely-ranging and diffuse group of processes has been very voluminous in the period under review and only a very small proportion of it can be cited in detail. Nevertheless, certain well-marked trends are to be noted, and these are continued from previous years. It is sometimes a little difficult to understand the incentives behind the proliferation of methods, often elaborate chemically, for

meeting a single and fairly simple functional requirement such as shower-proofing. There are very many suggestions for this; and it is becoming fashionable to exploit some of the increasingly complicated products from the expanding chemistry of organo–silicon compounds.

The inter-related effects in textiles of various qualities are still being discovered by the application of familiar principles. These qualities include dimensional stability, retention during washing and other wet treatments of mechanical finish such as glazing, wet strength, and resistance to creasing.

Cross-bonding by condensation of multi-functional molecules with and between the fibre molecules can be adjusted both to confer improved elasticity to the fibre and to diminish swelling in water. Swelling is also combated by causing the hydroxyl groups of cellulose to combine with groups which reduce their attraction for water. The original formaldehyde and formaldehyde–urea treatments are being replaced increasingly by formaldehyde–amino–triazine condensations, by glyoxal treatments and by treatments using more elaborate but essentially similar agents. Attention is being paid to processes in which the internal molecular arrangements of natural and manufactured cellulosic fibres are more or less disorganized by swelling agents and, after modification by mechanical stress, the new arrangement is set by heat and steam treatments. For stiff, impervious, embossed, or other effects, the textile is now coated or impregnated with a larger proportion of non-fibrous material than previously. These processes make use of an extremely wide range of substances, many suggested by the development of plastics chemistry for non-textile purposes. Probably the largest group of applications is that in which polyvinyl and polyacrylate derivatives are employed. Less is said this year than in previous ones about the application of cellulose ether derivatives in the production of stiffened and allied types of finish. The impetus given by the campaigns in South-East Asia to the search for efficient proofing agents against micro-biological and insect attack has not spent itself in post-war years, and there is a surprisingly large number of suggestions for rot- and mould-proofing treatments, paralleled by the insect proofing treatments which are more important for woollen textiles. The comments made above about shower-proofing seem to be applicable in this field also.

For those who desire to obtain a broad general picture of finishing developments during the past one or two decades, the Mercer Lecture delivered to the Society of Dyers and Colourists by E. Wilson[296] can be recommended. So also may a study by G. Cameron and T. H. Morton[297] on the cross-linking of regenerated cellulose fibres which results in the production of a number of different types of finish. Probably the most important single chemical in the production of the modern types of finish is formaldehyde, and I. J. Gruntfest and D. D. Gagliardi[298] have re-examined the interaction of this compound with cellulose under various conditions. The interaction products are most stable if formed at high temperatures and are then produced under fairly wide variations in acidity. At low concentrations of formaldehyde on the fibre, the formation of simple methylene ethers seems to be prodominant. With an excess of formadehyde present, a greater proportion combines and the

formation of polyoxymethylene ether cross-linkages is indicated. The effect of reaction with formaldehyde on the swelling, tenacity, elongation and crease-resistance of regenerated cellulosic fibres has also been examined systematically by Mlle. Goujet and le Chanoine Pinte.[299] Melamine–formaldehyde finishes have been of particular interest to the papermaker since they influence the fibre cementation and reduce the water uptake of cellulose and this improves the strength of the material to an extent which is proportionally much greater than with textiles. It is this function which has inspired an extensive examination of the colloidal properties of polymerized trimethylolmelamine dispersions, a study which is, however, also of interest to the textile finisher.[300]

Among the processes which may prove to lead to wider developments in formaldehyde treatments is the condensation with polymethylolphenol and cresols, by which the swelling in water is very greatly reduced, owing either to a complete shielding of the hydroxy-groups of cellulose or a cross-linking with this comparatively bulky condensate.[301–304]

Four processes, all seeming to differ in detail but all similar in principle, are interesting to compare as simple methods for reducing the swelling capacity of regenerated cellulose. In the first,[305] the usual method of prolonged steaming is improved by providing an inert atmosphere to protect the cellulose from oxidation. In the second, heating of the cellulose under pressure takes place after the water content has been carefully adjusted to the amount at which all the internal surfaces can be regarded as saturated with adsorbed water.[306] In the last two, pre-swelling to a limited extent by ammonia or amines is followed by the abstraction of water, either by heating[307] or by passage into hot organic liquids.[308] Closely allied to these four processes is one which consists of a mercerized finish in which the soda cellulose is steamed before washing takes place.[309]

It is interesting to find analogous processes, each with the same purpose, independently suggested, and applicable, the one to a natural fibre, the other to an artificial counterpart. The cottonization and consequent loss in strength of linen fabrics on repeated washing which, owing to the removal of the cementing hemicellulose and pectic materials from between the ultimates, is claimed to be minimized by a formaldehyde treatment which insolubilizes the cement.[310] The procedure is thus comparable to that in which flax-spun Fibro yarns are fibre-bonded with formaldehyde–resorcinol resins.[311]

In connexion with the reactions to which cellulose may be sumitted to form a basis for finishing effects, some extremely interesting work might be mentioned here. Cellulose (or polyvinyl alcohol) derivatives, such as the *p*-toluenechlorosulphonyl esters, have been cross-linked with true disulphide bonds; these bonds can be opened by mild reduction to give a soluble thiol form, and closed by mild oxidation to give insoluble disulphide forms.[312]

Improvements in finishing machinery are not generally novel or fundamental but consist in modifications in detail, for instance, improvements in air or hot gas circulation in drying or baking plants, better arrangements for cloth tension control in processing sensitive fabrics, the wide use of pneumatic or pneumatic-hydraulic systems for the more accurate control of nip pressures in calenders and mangles, etc. In the

design of pin-stenters, a most important item in light finishing of rayons, a version now in operation dispenses with the moving entry rails and uses a light articulated guiding unit with photoelectric selvedge detector and electronic operating relays, to feed the edge of the cloth, *via* a patent over-feed, to the non-swinging stenter rails.

This chapter, in view of the wide range of the subject-matter, has had to omit or to deal cursorily with many matters of great interest to the textile technologist. If a closer general view of the technology of textile processing is desired satisfaction may perhaps be found in the new joint venture of the Textile Institute and the Society of Dyers and Colourists who are publishing, at about the same time as this volume, a review of progress which is restricted to the various branches of fibre science and textile production.

References

[1] *J. Text. Inst., Manchr.*, 1949, **40**, P525
[2] *J. Soc. Dy. Col., Bradford*, 1949, **65**, 586
[3] *J. Text. Inst., Manchr.*, 1949, **40**, T527
[4] Ibid., P426
[5] Ibid., P857
[6] Ibid., P972
[7] *Indian J. agric. Sci.*, 1947, **17**, 305
[8] *Text. Res. J.*, 1948, **18**, 628
[9] Ibid., 1948, **18**, 679
[10] *Kunstseide u. Zellwolle*, 1949, **27**, 37
[11] *J. phys. colloid Chem.*, 1949, **53**, 260
[12] *Nature*, 1949, **163**, 19
[13] Ibid., 1948, **161**, 768
[14] *J. Textile Inst., Manchr.*, 1948, **39**, T1
[15] Ibid., T44
[16] *Nature*, 1949, **164**, 628
[17] FIAT Review of German Science, Biochem., Part III, 1948, 159
[18] Ibid., Preparative Org. Chem. Part III, 1948, 49
[19] *J. Text. Inst., Manchr.*, 1949, **40**, T715
[20] *Nature*, 1948, **162**, 665
[21] *Ind. Eng. Chem.*, 1948, **40**, 1711
[22] *Biochim. biophys. Acta*, 1949, **3**, 15
[23] *Proc. phys. Soc. Lond.*, 1949, **62B**, 257
[24] *J. phys. colloid Chem.*, 1948, **52**, 1197
[25] *Proc. Papermkrs.' Ass.*, 1947, **28**, 189, 211
[26] *Text. Res. J.*, 1949, **19**, 152
[27] *J. Text. Inst., Manchr.*, 1949, **40**, T831
[28] *C.R. Acad. Sci., Paris*, 1948, **226**, 1983, 1984
[29] *Bull. Soc. chim. Belg.*, 1948, **57**, 236
[30] *Nature*, 1948, **162**, 957
[31] *J. Text. Inst. Manchr.*, 1948, **39**, T351
[32] Ibid., 1948, **39**, T368
[33] *C.R. Acad. Sci., Paris*, 1948, **226**, 1987
[34] Ibid., **227**, 204
[35] Ibid., **226**, 1528
[36] *Kunstseide u. Zellwolle*, 1948, **26**, 86
[37] *C.R. Acad. Sci., Paris*, 1948, **227**, 529
[38] *J. Soc. chem. Ind. Japan*, 1941, **44**, 1057; *Chem. Abs.*, 1949, **43**, 1962b
[39] *Science and Culture*, 1948, **14**, 123; *Chem. Abs.*, 1949, **43**, 2429c
[40] *Indian J. Phys.*, 1948, **22**, 141
[41] *Boll. Cotoniera*, 1941, **36**, 453; *Brit. Abs.*, 1948, C, 260
[42] B.P. 618,584

[43] *Text. Age*, 1948, **12** (7), 10, 11, 14; *J. Soc. Dy. Col., Bradford*, 1949, **65**, 265
[44] *Text. Res. J.*, 1948, **18**, 155
[45] *Svensk Papperstidning*, 1949, **52**, 157
[46] *Text. Res. J.*, 1948, **18**, 149
[47] *J. appl. Chem., USSR*, 1949, **21**, 1037
[48] Ibid., 1073
[49] *Text. Res. J.*, 1948, **18**, 387
[50] *Makromol. Chemie*, 1948, **2**, 298
[51] *Svensk Papperstidning*, 1949, **52**, 61, 107
[52] *Trans. Faraday Soc.*, 1948, **44**, 941
[53] *J. chem. Soc.*, **1949**, 1536
[54] B.P. 605,367; U.S.P. 2,448,892
[55] *J. Amer. chem. Soc.*, 1949, **71**, 2200
[56] *J. Text. Inst., Manchr.*, 1947, **38**, T389
[57] *J. chem. Soc.*, **1948**, 1135
[58] *J. appl. Chem. USSR*, 1949, **22**, 857
[59] Davidson, G. F. and Nevell, T. P., *J. Textile Inst., Manchr.*, 1948, **39**, T59
[60] Wilson, K., *Svensk Papperstidning*, 1948, **51**, 45
[61] van der Wyk, A. J. A. and Studer, M., *Helv. chim. Acta*, 1949, **32**, 1698
[62] Krajčinovič, M., *Arhiv. Khem. Technol.*, 1947, **19**, 101, *see J. Soc. Dy. Col., Bradford*, 1949, **65**, 262
[63] Segal, L., Trip, R. C., Trip, V. W. and Conrad, C. M., *Analyt. Chem.*, 1949, **21**, 712
[64] Windeck-Schultze, K. and Peiper, J., *Textilberichte*, 1948, **29**, 20
[65] *J. Soc. Dy. Col., Bradford*, 1949, **65**, 748
[66] Ibid., 1949, **65**, 758
[67] *J. Amer. chem. Soc.*, 1949, **71**, 958,
[68] *Text. Res. J.*, 1948, **18**, 350
[69] *J. Soc. Dy. Col., Bradford*, 1949, **65**, 56
[70] *Aust. J. Sci.*, 1948, **11**, 60, 61; *Chem. Abs.*, 1949, **43**, 1181c
[71] *Nature*, 1949, **163**, 877
[72] *Mem. Services chim. État. Paris*, 1947, **33**, 95; *J. Soc. Dy. Col., Bradford*, 1949, **65**, 573
[73] *Text. Res. J.*, 1948, **18**, 749
[74] *Angew. Chem.*, 1948, **A60**, 46
[75] *J. Soc. chem. Ind. Japan*, 1942, **45**, 1122, 1126, 1128; *Chem. Abs.*, 1949, **43**, 1936d
[76] *Ind. Eng. Chem.*, 1948, **40**, 1500
[77] Hamalainen, C. and Reed, J. D., ibid., 1949, **40**, 1018
[78] B.P. 620, 726; B.P. 616, 132
[79] British Celanese Ltd., B.P. 608,310
[80] Idem, B.P. 609,790
[81] Gardner, T. S. and Eastman Kodak Co., U.S.P. 2,461,152
[82] Allen, J. J. and Hawkes, J. A., B.P. 617,931
[83] *J. gen. Chem., Moscow*, 1948, **18**, 1692
[84] American Viscose Corpn. and Richter, G. A., B.P. 614,659
[85] Urbanshi, T., *Bull. Soc. chim. Belg.*, 1948, **57**, 467
[86] Yashunskaya, A. G., Shorygina, N. N. and Rogovin, Z. A., *J. appl. Chem., USSR*, 1949, **22**, 865
[87] Campbell, H. and Johnson, P., *J. Polymer. Sci.*, 1948, **3**, 735
[88] Reprint, Textile Institute, Nov., 1949
[89] *Bull. Soc. chim. Belge*, 1948, **57**, 263
[90] *Svensk Papperstidning*, 1948, **51**, 52
[91] Ibid., 1948, **51**, 199
[92] Ibid., 509
[93] Ibid., 537
[94] Ibid., 254
[95] *J. Amer. chem. Soc.*, 1949, **71**, 1023
[96] *Svensk Papperstidning*, 1949, **52**, 165
[97] Hercules Powder Co., Klug, E. D. and Tinsley, J. S., B.P. 623,276
[98] Reid, J. D. and Daul, G. C., *Text. Res. J.*, 1948, **18**, 551
[99] Brown, R. L. and Du Pont, U.S.P. 2,462,159
[100] Signaigo, F. K. and Du Pont, U.S.P. 2,459,547
[101] *Text. Res. J.*, 1948, **18**, 643

[102] *Mém. Services chim. État, Paris*, 1947, **33**, 159, 169
[103] Ringstrom, E. and Apler, N. H., *Svensk Papperstidning*, 1948, **51**, 501
[104] *J. appl. Chem., USSR*, 1949, **22**, 625
[105] Scherer, P. C. and Phillips, R. W., *Rayon synth. Text.*, 1949, **30** (5), 45, 53
[106] *Kolloidzschr.*, 1945, **110**, 26
[107] *J. Polymer Sci.*, 1948, **3**, 487, 834
[108] *Research*, 1949, **2**, 486
[109] Teunissen, P. H., *Svensk Papperstidning*, 1948, **51**, 497
[110] Kleinert, Th. and Mössmer, V., ibid., 1948, **51**, 541
[111] Samuelson, O., ibid., 1948, **51**, 331
[112] *Rec. Trav. chim. Pays-Bas*, 1948, **67**, 983
[113] *Kunstseide u. Zellwolle*, 1948, **26**, 244
[114] *J. Tex. Inst., Manchr.*, 1948, **39**, T148
[115] Ibid., 1949, **40**, T327
[116] *Text. Rdsch.*, 1949, **4**, 117
[117] *Text. Res. J.*, 1948, **18**, 366
[118] N.V. Onderzoekingsinstituut 'Research,' B.P. 606,295, 607,330
[119] Lustrafil Ltd. and Barker, S. W., B.P. 608,435
[120] American Viscose Corpn. and Truitt, J. A., B.P. 615,140
[121] American Viscose Corpn. and Furness, W. H., B.P. 608,781
[122] Harbens, Ltd. and Leon, M., B.P. 614,116
[123] Industrial Rayon Corpn. of America, *Text. Wkly.*, 1948, **42**, 1290
[124] Algemeene Kunstzijde Unie N.V., B.P. 617,109
[125] *Fibres*, 1948, **9**, 379
[126] Heberlein and Co. A.-G., B.P. 606,257
[127] Cuprum Soc. Anon., B.P. 606,983
[128] Stökly, J. J., B.P. 612,198
[129] Sisson, W. A. and American Viscose Corpn., U.S.P. 2,443,711
[130] Woodell, R. and Du Pont, U.S.P. 2,462,927
[131] London: Sylvan Press, 1949
[132] H.M. Stationery Office
[133] British Celanese Ltd., B.P. 607,993
[134] Barrington, T. F., B.P. 619,564
[135] Brit. Celanese Ltd., B.P. 615,342
[136] Idem, B.P. 616,133
[137] *J. Soc. Dy. Col., Bradford*, 1950, **66**, 9
[138] *J. Text. Inst. Manchr.*, 1949, **40**, T590
[139] Courtaulds Ltd. and Tallis, E. E., B.P. 605,826
[140] Courtaulds, Ltd., Tallis, E. E. and Clotworthy, H. R. S., B.P. 624,987
[141] *Nature*, 1948, **162**, 225
[142] Ibid., 1949, **164**, 110
[143] Alginate Industries Ltd., Speakman, J. B., Chamberlain, N. H. and Dorkin, C. M. C., B.P. 621,362
[144] *J. Text. Inst., Manchr.*, 1949, **40**, T299
[145] Ibid., 1949, **40**, P532
[146] *Text. Industr.*, 1948, **112** (11), 127
[147] Ibid., 1949, **113**, (3), 131
[148] Axford, L. and United States Rubber Co., U.S.P. 2,471,554
[149] Stein, Hall and Co. Inc., B.P. 614,137
[150] U.S.P. 2,443,512
[151] Atlas Powder Co., B.P. 612,440
[152] British Celanese Ltd., B.P. 614,298
[153] British Nylon Spinners Ltd., Loasby, G. and Munden, A. R., B.P. 615,185
[154] Kiviat, F., B.P. 605,866
[155] Smith, R. J. and I.C.I. Ltd., B.P. 610,167–9
[156] *Text. Rdsch.*, 1949, **4**, 114
[157] Bourne, E. J., Haworth, N., Macey, A. and Peat, S., *J. chem. Soc.*, **1948**, 924
[158] Meyer, K. H., Bernfeld, P., Rathgeb, P. and Gürtler, P., *Helv. chim. Acta*, 1948, **31**, 1536
[159] Bourne, E. J., Sitch, D. A. and Peat, S., *J. chem. Soc.*, **1949**, 1448
[160] *J. Amer. chem. Soc.*, 1949, **71**, 128
[161] *Cereal Chem.*, 1949, **26**. 239

[162] Le Meuse, E. H., Van Lanen, J. M. and U.S. Secretary of Agric., U.S.P. 2,451,567
[163] Blaisten, R. J., *Rev. Asoc. bioquim. Argentina*, 1948, **15**, 47; *Chem. Abs.*, 1949, **43**, 1571
[164] Klyucharev, S., *Tekstil. Prom.*, 1948, **8** (3), 26
[165] *Chem. & Ind.*, **1948**, 51
[166] *Text. Res. J.*, 1948, **18**, 42
[167] *J. biol. Chem.*, 1949, **178**, 207
[168] Derham, L. J., B.P. 608,468
[169] Madsen, L. T. S., B.P. 607,274
[170] Hall Laboratories and Albright & Wilson Ltd., B.P. 610,201
[171] Pieters, H. A. J., *Analyt. chim. Acta*, 1948, **2**, 272
[172] *Rev. Industr. text. Belge*, 1948, No. 26, 12
[173] Shiraeff, D. A., *Amer. Dyest. Rep.*, 1948, **37**, 411
[174] Barr, T., Oliver, J. and Stubbings, W. V., *J. Soc. chem. Ind.*, 1948, **67**, 45
[175] With Cushman, A. and Brady, A. P., *J. Colloid Sci.*, 1948, **3**, 425
[176] With Marsden, S. S., *Acta Crystall.*, 1948, **1**, 270
[177] With Hoffman, O. A., *J. phys. colloid Chem.*, 1949, **53**, 39
[178] With Sierichs, W. M., *J. Amer. Oil Chem. Soc.*, 1948, **25**, 221
[179] *Nature*, 1949, **163**, 767
[180] *Analyt. Chem.*, 1949, **20**, 1039
[181] Dixon, J. K., Weith, A. J., Argyle, A. A. and Salley, D. J., *Nature*, 1949, **163**, 845
[182] A.A.T.C.C., Midwest Section, *Amer. Dyest. Rep.*, 1948, **37**, P596
[183] Bayley, C. H., Weatherburn, A. S. and Rose, G. R. F., *Laundry and Dry Cleaning J.*, 1948, Dec.
[184] Nieuwenhuis, K. J., Communication No. 66, Laundry Experimental Station, Delft; *J. Text. Inst., Manchr.*, 1949, **40**, A30
[185] Voss, J., *Textilberichte*, 1948, **29**, 382; 1949, **30**, 197
[186] Viertel, O., ibid., 1947, **28**, 345
[187] Bartholomé, E. and Buschman, K., ibid., 1949, **30**, 249
[188] Gibson, M., *J. Soc. chem. Ind.*, 1948, **67**, 337
[189] Water Pollution Research, Tech. Paper No. 10, D.S.I.R.
[190] Asai, I. *et al.*, *J. agric. Soc., Japan*, 1943, **19**, 102, 566; 1944, **20**, 211; *Chem. Abs.*, 1949, **43**, 1984
[191] University of Minnesota, B.P. 615,519
[192] *J. Text. Inst., Manchr.*, 1948, **39**, T274
[193] *Science and Culture*, 1943–4, **9**, 451; *Chem. Abs.*, 1948, **42**, 7532
[194] Lesslie, C., Hagan, L., Guthrie, J. D., *Analyt. Chem.*, 1949, **21**, 190
[195] Hudson, R. E. and Waddle, H. M., *Text. Res. J.*, 1948, **18**, 232
[196] Mathieson Alkali Works, with Carr, R. L. and Synan, J. F., B.P. 607,916
[197] Idem, with Vincent, G. P. and Dubeau, L., U.S.P. 2,469,249
[198] Idem, with Vincent, G. P. and Dubeau, L., B.P. 611,939
[199] Idem, with Carr, R. L., B.P. 611,966
[200] O'Keefe, G. W. and Proctor and Schwartz Inc., U.S.P. 2,443,990
[201] B.P. 611,589
[202] Bloch, R., Goldschmidt, K., Goldschmidt, P., Schnerb, I., Palestine Potash Ltd., B.P. 615,604
[203] *Textilberichte*, 1948, **29**, 57, 96, 133
[204] *Tekstil. Prom.*, 1947, **7** (12), 23
[205] Mathieson Alkali Works with Tatomer, H. N., B.P. 625,201
[206] Idem, with Carr, R. L., B.P. 608,547
[207] Scanlan, J. T., Stirton, A. J., Swern, D. and Roe, E. T., *Amer. Dyest. Rep.*, 1949, **38**, 455
[208] B.P. 615,132
[209] Kenyon, R. L., Hasek, R. H., Davy, L. G. and Broadbrooks, K. J., *Ind. Eng. Chem.*, 1949, **41**, 2
[210] *Text. Res. J.*, 1948, **18**, 298
[211] *Amer. Dyest. Rep.*, 1948, **37**, 213; 1949, **38**, P9
[212] *Text. Res. J.*, 1948, **18**, 615
[213] Williams, S. H., B.P. 609,728
[214] *J. Soc. Dy. Col., Bradford*, 1949, **65**, 381
[215] Bendiktov, D., *Tekstil. Prom.*, 1948, **8** (6), 44
[216] B.P. 620,584

[217] Converse, S., U.S.P. 2,441,992
[218] Spooner, W. W., B.P. 619,539
[219] *J. Soc. Dy. Col., Bradford*, 1950, **66**, 17
[220] A.A.T.C.C.. New York Section, *Amer. Dyest. Rep.*, 1949, **38**, P442
[221] *J. Soc. Dy. Col., Bradford*, 1949, **65**, 145
[222] *J. Text. Inst., Manchr.*, 1949, **40**, P583
[223] *J. Soc. Dy. Col., Bradford*, 1949, **65**, 352
[224] *Amer. Dyest. Rep.*, 1948, **37**, P435
[225] *Techn. Bull. (Du Pont)*, 1946, **2**, 116; U.S.P. 2,318,133, *J. Text. Inst., Manchr.*, 1949, **40**, A239
[226] Ibid., 1949, **5**, 8; *J. Text. Inst., Manchr.*, 1949, **40**, A484
[227] *Textilberichte*, 1947, **28**, 93, 136
[228] *J. Soc. Dy. Col., Bradford*, 1949, **65**, 508
[229] *J. Text. Inst., Manchr.*, 1949, **40**, T57
[230] Ibid., T175
[231] Hadfield, H. R. and Sharing, D., *J. Soc. Dy. Col., Bradford*, 1948, **64**, 381
[232] Textron Incorp. and Galatioto, L. C., B.P. 613,588
[233] Sutton, G. D. and T. E. Marchington and Co., B.P. 612,078
[234] Idem, B.P. 622,676
[235] British Celanese Ltd,, Olpin, H. C. and Jackson, T., B.P. 614,600
[236] British Celanese Ltd., B.P. 626,740
[237] Haddock, N. H., *Research*, 1948, **1**, 685
[238] Haddock, N. H., Wood, C and I.C.I. Ltd., B.P. 619,035
[239] General Aniline and Film Corpn. and Fox, A. L., B.P. 614,407
[240] Coffey, S. H., Haddock, N. H., Lodge, F., Wardleworth, J., Wood C. and I.C.I. Ltd., B.P. 613,980–82–83
[241] Douglas, G. T., Parkinson, A., Wakefield, H. and I.C.I. Ltd., B.P. 603,753
[242] *J. appl. Phys.*, 1948, **19**, 1097
[243] Landolt, A., *Text. Rdsch.*, 1948, **3**, 376
[244] Caspar, E., ibid., 1947, **2**, 212; *J. Soc. Dy. Col., Bradford*, 1950, **66**, 177
[245] Peterson, S., *Angew. Chem.*, 1949, **1**, 17
[246] Melson, H. E. and Stearns, E. I., *Amer. Dyest. Rep.*, 1948, **37**, 423
[247] *J. Text. Inst., Manchr.*, 1948, **39**, T285
[248] Ibid., T293, T305; *Text. Res. J.*, 1948, **18**, 659; *J. Soc. Dy. Col., Bradford*, 1948, **64**, 336
[249] Bourne, E. J. *et al.*, *J. chem. Soc.*, **1948**, 1687
[250] Idem, *Nature*, 1948, **161**, 762
[251] Idem, *J. chem. Soc.*, **1949**, 1
[252] Idem, ibid., 5
[253] Hirst, E. L. *et al.*, *Biochem. J.*, 1948, **43**, 70
[254] Idem, *J. chem. Soc.*, **1948**, 1779
[255] Meyer, K. H. and Rathgeb, P., *Helv. chim. Acta*, 1948, **31**, 1533, 1545; 1949, **32**, 1102
[256] Krishnaswamy, K. G. and Sreenivasan, A., *J. biol. Chem.*, 1949, **178**, 1253
[257] Potter, A. L. and Hassid, W. Z., *J. Amer. chem. Soc.*, 1948, **70**, 3488, 3774
[258] Higginbotham, R. S. and Morrison, G. A., *J. Text. Inst., Manchr.*, 1949, **40**, T201, T208, T783
[259] de Willigen, A. H. A., Hofstee, J. and de Groot, P. W., *Chem. Weekbl.*, 1948, **44**, 422
[260] Whistler, R. L. and Johnson, C., *Cereal Chem.*, 1948, **25**, 418
[261] Krajčinovič, M., *Arhiv. Khem. Technol.*, 1947, **19**, 104; *Brit. Abs.*, 1949, C, 35
[262] Meyer, K. H. *et al.*, *J. Phys. colloid Chem.*, 1949, **53**, 319
[263] *J. Soc. Dy. Col., Bradford*, 1949, **65**, 434
[264] *Textilberichte*, 1949, **30**, 154
[265] *Amer. Dyest. Rep.*, 1949, **38**, 663
[266] Ibid., P69
[267] *Tekstil. Prom.*, 1949, **9**, 27; *J. appl. Chem., USSR.*, 1948, **21**, 685
[268] Douglas, G. T. *et al.* and I.C.I. Ltd., B.P. 612,892
[269] Brit. Indust. Plastics Ltd. and Horobin, A. L., B.P. 614,046
[270] Douglas, G. T. *et al.* and I.C.I. Ltd., B.P. 622,967
[271] Ciba Ltd., B.P. 614,266
[272] Du Pont, Dahlen, M. A. and Shows, M. O., B.P. 620,791
[273] La Piana, F. G. *et al.* and Stein, Hall & Co., U.S.P. 2,453,752

[274] Du Pont, Shows, M. O. and Meunier, P. L., B.P. 626,581
[275] Courtaulds Ltd., Boulton, J. *et al.*, B.P. 625,215
[276] Idem, B.P. 625,609
[277] Hardy, W. B., Hardy, E. M. and Amer. Cyanamid Co., U.S.P. 2,466,656
[278] Pelton, E. L., Hutchinson, C. O. and Dow Chem. Co., U.S.P. 2,445,632
[279] Durand and Huguenin A.-G., B.P. 605,696
[280] Douglas, G. T., McQueen, S. T. and I.C.I. Ltd., B.P. 618,616
[281] Geigy J. R., A.-G., B.P. 616,950
[282] Ciba Ltd., B.P. 604,690
[283] Schofield, A., B.P. 604,090
[284] *Techn. Bull.* (*Du Pont*), 1947, **3**, 5; *J. Text. Inst., Manchr.*, 1949, **40**, A241
[285] Miller, C. F. and Du Pont, U.S.P. 2,468,940
[286] Vickerstaff, T. and I.C.I. Ltd., B.P. 609, 944
[287] Hardacre, R. W. and I.C.I. Ltd., B.P. 626,419
[288] Cheskova Ltd., B.P. 620,629
[289] Walker, D. and David Evans & Co., Ltd., B.P. 625,108
[290] Künzl, R., *Textilberichte*, 1949, **30**, 29, 67
[291] Pioneer Screen Printers Ltd., *Text. Merc.*, 1949, **120**, 671
[292] Établ. Schaeffer et Cie., B.P. 610,115
[293] Idem, B.P. 618,016
[294] Huebner, W. C., B.P. 615,556: 618,513
[295] Goss Printing Press Co. Ltd., B.P. 619,224
[296] *J. Soc. Dy. Col. Bradford*, 1949, **65**, 497
[297] Ibid., 1948, **64**, 329
[298] *Text. Res. J.*, 1948, **18**, 643
[299] *Textiles* (*Bull. Inst. Text. France*), 1948, No. 6, 25
[300] Dixon, J. K. *et al.*, *Paper Tr. J.*, 1948, **127**, *TAPPI*, 455
[301] Comptoir des Textils Artificiels, B.P. 611,310
[302] *Kunstseide u. Zellwolle*, 1948, **26**, 114
[303] Hall, A. J., *Silk and Rayon*, 1948, **22**, 1689
[304] N.V. Onderzoekingsinstituut 'Research,' B.P. 603,881
[305] Comptoir des Textiles Artificiels, B.P. 615,264
[306] N.V. Onderzoekingsinstituut 'Research,' B.P. 603,863
[307] Moore, H. B., *Text Res. J.*, 1948, **18**, 749
[308] U.S. Rubber Co., B.P. 608,292
[309] Bener, C., B.P. 615,741
[310] Richer, A., *Textilberichte*, 1947, **28**, 129
[311] *Textile Recorder*, 1949, **66**, No. 792, 61
[312] Izard, E. F. and Morgan, P. W., *Ind. Eng. Chem.*, 1949, **41**, 617

THE PROTEIN FIBRES

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THIS chapter reviews recent work and advances on the applied chemistry of wool, silk, synthetic polypeptides, regenerated protein fibres and fibres from polyamides, polyesters and other polymers.

The shrinkage and felting of wool continue to receive much attention, while industrial research reports disclose considerable activity in the fields of scouring and dyeing, particularly attempts to dye continuously. Synthetic detergents continue to replace the soap–soda ash systems. Important contributions towards knowledge of the fundamental structure of fibrous proteins have been made by those investigators in the field of synthetic polypeptides. Studies on the regenerated protein fibres include work on regenerated wool fibres and details of the zein fibre recently marketed in U.S.A. Among the polyamide and polyester fibres, search continues for dyeing techniques of improved fastness. In the former class, patents and papers indicate methods for producing greater fibre elasticity, including the recently introduced elastic nylon.

Wool

Shrinkage and felting

Frishman *et al.*[1] have investigated the reaction between wool and chlorine at p_H 1·0, p_H 3–7 and p_H 9–11. Low p_H treatment resulted in a loss of weight and destruction of surface scale structure. Intermediate p_H range showed extensive fibre modification with low cystine content and high alkali solubility, while treatment at p_H 9–11 resulted only in minor modifications of the wool protein. It was further shown that wool treated with hypochlorite solutions at p_H 8–9 may be rendered shrink-resistant with a minimum of fibre modification. Under most of these conditions the rate of dyeing was increased; mild conditions of treatment decreased the rate of dyeing.

Recent observations were made on the mechanism of the anti-shrink action of chlorine, potassium hydroxide and sulphuryl chloride on wool by Farnworth, Neish and Speakman[2,3] who worked on the principle that if unshrinkability is caused by disulphide bond breakdown then conversion of –S–S– links to less reactive cross-linkages should prevent shrinkage. Four types of modified wool were examined in which the –S–S– link had been replaced by:

(1) $-CH_2{\cdot}S{\cdot}Hg{\cdot}S{\cdot}CH_2-$
(2) $-CH_2{\cdot}S(CH_2)_3{\cdot}S{\cdot}CH_2-$
(3) $-CH_2{\cdot}S{\cdot}CH_2-$ (using alkali), and
(4) $-CH_2{\cdot}S{\cdot}CH_2-$ (using potassium cyanide).

In all cases, the modified wool was more difficult to make unshrinkable than the untreated wool. More successful results were obtained in (3)

and (4) than in (1) and (2) and the conversion of disulphide bonds into lanthionine cross-linkages inhibited completely the anti-shrink action of chlorine, sulphuryl chloride and potassium hydroxide. These experiments would seem to leave no doubt that these reagents make normal wool unshrinkable by causing disulphide bond breakdown in the surface of the fibres.

It has been found[4] that the anti-shrink action of sulphuryl chloride on wool is considerably impaired when residual oil and soap are removed from commercial flannel by solvent extraction. High reactivity can be restored if sodium oleate or oleic acid is added to the purified flannel from an alcoholic solution. The conclusion was reached that the active compound is an organic peroxide in the oleic acid and it was determined that benzoyl peroxide has the same effect as oleic acid in assisting the reaction between sulphuryl chloride and the –S–S– bonds of wool.

Alexander, Carter and Hudson[5] have recently shown that wool can be rendered non-felting by treatment with dilute solutions of permanganate at a $p_H < 2$. Treated wool does not felt when given prolonged treatments in a washing machine, but felts as much as untreated wool when given a milling action. The reaction mechanism involves oxidation of the –S–S– bond and the damage done to the wool by the permanganate treatment is slight.

Another method[6] of promoting anti-felt action of wool involves the treatment of wool fabric of normal regain with a compound such as methyl trichlorosilane in carbon tetrachloride. Area shrinkage of the fabric is reduced from 25% to 4%, and the deposit cannot be removed by repeated launderings. Additional work[7] has shown that to obtain non-feltability with a deposit of less than 5%, (1) the polymer must be produced from a monomer containing a reactive grouping, such as Si–Cl, groupings such as $SiOC_2H_5$ and $Si–NH_2$ not being satisfactory; and (2) the polymer must be a hard solid. Evidence is given that the polymer is initially anchored to the fibres by means of –Si–NH linkages.

It has been claimed[8] that shrinkage of woollen materials is reduced by impregnation with a resinous vinyl polymer. In one example using methyl methacrylate, a firm deposit of 22% resin was obtained and in a laundering test a treated pattern shrank 6% while a control pattern shrank 35%.

Lipson and Speakman[9] present further information on the formation of polymers in wool. Both samples of loose wool and of flannel were used in the investigations. These were impregnated with ferrous ammonium sulphate, dried and then treated with a solution of methacrylic acid containing a trace of hydrogen peroxide. Preferential internal polymerization was also obtained with methyl methacrylate or copolymers of methyl methacrylate and methacrylic acid by an emulsion technique. Wool treated in this way possesses modified dyeing properties, increased wear resistance, and reduced shrinkage. An interesting and important reaction is obtained with methacrylamide polymerization followed by cross-linking with formaldehyde, when a large increase in the resistance of the treated wool fibres to extension in water is produced.

A limited amount of cross-linking[10] causing an appreciable reduction

in milling shrinkage of flannel is brought about by treatment with 3 : 4-*iso*propylidene-1 : 2-5 : 6-dianhydromannitol for 24 hours at 50° C. Reaction is presumed to take place with the carboxyl groups of salt linkages and as the scaliness of the wool fibre is unaltered the reduction in shrinkage must be due to modified elastic properties of the fibres.

Wool shrinkage control with thermosetting resins is described by Fluck,[11] who treated wool before dyeing with hydrogen peroxide and a resin colloidal solution which was thoroughly dried on to the fabric. The colloidal solution used was prepared from a melamine–formaldehyde reaction product and acetic acid followed by ageing. Plant trials indicate that fabrics so treated have excellent shrinkage control and bright, clear colours including pastel shades may be safely used.

The function of methylated melamine resins in controlling the shrinkage of woollen fabrics is discussed by Stock and Salley.[12] Examination of fibres from treated fabrics was made from the following viewpoints, since felting shrinkage has normally been ascribed to any or all of these conditions : (*a*) alteration in hysteresis response of fibres to stress, (*b*) change in friction between contiguous fibres and (*c*) a bonding of neighbouring fibres to form a network of restricted relative movement. (*a*) was ruled out and under (*b*) a significant decrease in the directional coefficient of friction as a result of resin treatment was found for treated single fibres, but not for fibres withdrawn from treated cloths. Tensile strength values of felts made from untwisted single threads from treated cloth are significantly increased by resin treatment. The conclusion, therefore, was that the resin acted as a bonding agent between neighbouring fibres.

Patent claims[13] are made protecting the anti-felting and bleaching action on wool of small amounts of copper, nickel, silver or mercury with subsequent treatment with solutions of peroxides. The production of non-felting wool by means of exposure to ultrasonic vibrations, and the non-felting of wool/cellulose acetate fabrics are also covered by other patent specifications.[14,15]

Other patents covering unshrinkable finishes for woollen materials include treatments with methylolurea,[16] butadiene polymers and copolymers,[17] methylolmelamine resins containing insecticide[18] and methylated methylolmelamine plus a silicofluoride[19] to produce resistance to black carpet beetle larvae. Other processes include the treatment of wool in caustic alkali solution containing accelerators such as hydrosulphides, etc.[20] and the action of a water soluble bromate,[21] and calcium hypochlorite.[22] Alkaline hypochlorites are also claimed[23] for imparting shrink resistance to flannel shirting and wool blankets, and mixed and rayon-worsted fabric.

Supercontraction

Speakman[24] contends that cystine breakdown in wool causes supercontraction and that permanent set may be accounted for by the formation of new linkages of the type –S–NH.[25]

Blackburn and Lindley[26] have recently investigated the setting and supercontraction of wool fibres under varying conditions of p_H and temperature. During this work it was discovered that esterified wool

supercontracts to a lesser extent than untreated fibres and is more readily set. There seemed to be more evidence for the presence of $-\overset{|}{\underset{|}{C}}-S-\overset{|}{\underset{|}{C}}-$ linkages in alkali-treated wool as combined lanthionine rather than S–NH linkages. These authors are more inclined to shift the emphasis, in the setting of wool in mildly alkaline buffers at 100° C., off the sulphur linkages and on to the salt linkages and hydrogen bonds. The explanation of the smaller degree of supercontraction of methylated wool fibres may be found in a change of the force tending to cause supercontraction; it may be dependent on the positive charge of the methylated fibre relative to that of the untreated fibre.

Deaminated wool[27] behaves similarly to untreated wool with mildly alkaline buffers at 100° C. and lanthionine is formed. With stronger alkalis, unlike untreated wool, deaminated wool yields no lanthionine. Physical properties of deaminated wool confirm earlier observations of Speakman. If, however, the setting of wool fibres by alkali treatment is attributed to the formation of lanthionine cross-linkages, no explanation is afforded of the failure to set and the supercontraction of deaminated fibres. In this paper[27] further evidence is presented to support the physical mechanism of set postulated by Blackburn and Lindley above.

Elöd and Zahn[28] have shown that wool supercontracts in hot concentrated solutions of phenol and formamide without disulphide-bond attack, indicating a mechanism involving hydrogen bonds. More recently these workers[29] found that wool keratin supercontracted either by Speakman's method or by phenolic solutions does not develop any special X-ray diagram associated with the supercontracted state. If cystine linkages are also broken by treatment with resorcinol etc. increased supercontraction takes place. It was also shown that silk and polyamides which do not contain cystine cross-linkages undergo supercontraction in phenolic solutions.[30]

Strong solutions of lithium bromide are sufficiently good hydrogen bond breakers to dissolve silk and polypeptides. Alexander[31] using 100% lithium bromide solution found that wool undergoes reversible supercontraction without swelling or damaging the wool. Under certain p_H conditions the supercontraction is irreversible. The fact that after alkali treatment a wool no longer supercontracts in a boiling solution of bisulphite but still contracts in a solution of lithium bromide indicates that two mechanisms are involved in supercontraction, one a disulphide breakdown and the other a hydrogen bond breakdown. Further work is obviously desired on this topic and Alexander has indicated that he will attempt to evaluate the relative importance of these two links in this connection.

Modifications of wool: combination with acids and dyes

Recent work by Peters and Speakman[32] reviews the theories of Steinhardt and Harris and Gilbert and Rideal on acid/wool combination and compares these with the Donnan membrane equilibrium theory. A quantitative interpretation of the combination of wool with HCl, H_2SO_4 and HCl in presence of KCl has been obtained in terms of the Donnan

theory. The 'internal' p_H is calculated and when the amount of combined acid is plotted as a function of this, then the mid-point of the titration curve is found to be between 4·15 and 4·35 in the case of HCl. This would be expected if combination were due to back-titration of the carboxyl groups of salt linkages. These authors conclude that 'the Donnan theory is capable of giving a more precise interpretation of the titration curves than the expressions derived from other considerations by Steinhardt and Harris and Gilbert and Rideal.' Kitchener and Alexander[33] give reasons for arriving at the opposite view that the Donnan theory does not shed new light on the acid/wool equilibrium and is less powerful than the Gilbert and Rideal theory. Replying to this attack, Peters and Speakman[34] assert that the calculation of 'internal' p_H is a step forward in this rather complex problem.

Modifications of wool

Kirst[35] has found that wool methylated by means of an ethereal solution of diazomethane has decreased strength and alkali resistance. The original and methylated wools were reduced with calcium thioglycollate and then treated with 1 : 3-bischloromethyl-4 : 6-dimethylbenzene. The reaction of the reduced wool with this dichloro compound was more effective in increasing alkali resistance in the case of the original wool than with the methylated wool.

If wool is treated with the difunctional diazo compound bisdiazohexamethylene, alkali resistance is increased owing to the formation of new cross linkages. Kirst[36] also treated wool with compounds such as hexanediol bischloromethyl ether and found an increased alkali resistance and a decrease in felting when washed. It was reckoned that methylene or polymethylene groups are formed between the polypeptide chains. He also investigated[37] the use of *s*-dichloracetone and 1 : 3-bischloromethyl-4 : 6-dimethylbenzene as cross-linking agents using the Harris method of first reducing the wool, and found the decrease in alkali solubility to be the same as with dibromoethane.

Speakman's method of reducing wool with sodium bisulphite and re-linking with metal salts was modified by using calcium thioglycollate as the reducing agent. The zinc salt gave a product which did not yellow with hot alkali and seemed to be of some technical interest. Elöd and Zahn[38] have studied various properties of these wools modified by the Kirst method. They found the treated wool to have greater resistance to mechanical deformation but a lower breaking load. Supercontraction measurements in various media show that the treated wool possesses increased resistance to chemical reagents. Similar alkali solubility effects can be obtained with di- or polyethyleneimine derivatives[39] on the wool fibre.

Chemical composition of keratin

Stoves[40] has suggested that the medulla present in coarser wools contains a lipoprotein–cholesterol complex. Medullary keratin has a greater affinity for basic dyes than cortical keratin. Blackburn[41] has also studied medullated and non-medullated types of wool. No evidence was found for a phosphatide in medullary cells. Medullated wool

showed a rather lower cystine content. More glutamic acid, aspartic acid, and basic amino-acids were found to be present in medulla than cortex. In porcupine quill medullary cells it appears that the medulla (β-keratin) contains a higher proportion of amino-acids with short non-polar side chains than does the cortex (α-keratin), which has a larger amount of bulky side-chains.

Lindberg and Gralen[42] by means of electron-microscope studies show that on wool surface there is a chemically resistant membrane about 100 A. thick, an intermediate layer and the scale shields. Frictional behaviour of wool and change with various reagents may now be partially explained by the histological structure of the wool outer layers.

Frictional properties of wool fibres

A survey of work on the frictional properties of wool fibres recently carried out in some detail by Lindberg and Gralen,[79] Makinson[80] and Frishman, Smith and Harris[81] together with earlier investigations has, owing to lack of space, been left over from this year's review.

Wool technology

Scouring and bleaching

Interest is still pronounced in the replacement of soap by synthetic detergents for wool scouring.

A laboratory method for evaluating detergents used in a continuous-flow wool scouring system is described by Leonard and Winch[43] and involves rapid extraction by carbon tetrachloride of residual grease in dried scoured skeins. Using this method[44] the following types of detergent were tested : sodium fatty alcoholic sulphonate, alkyl aryl sulphonate, non-ionic polyethylene oxide condensate, cake soap and liquid coco-nut oil soap. Only the polyethylene oxide condensate showed promise of competing economically with the tall oil soap–soda ash standard.

It has been reported[45] that scouring with sulphonated fatty alcohols allows of a more rapid feed of wool than in a soap–soda bath. The elasticity of wool fibres after washing treatments in sodium carbonate and other alkaline detergents showed a loss of about 40–60%.

La Fleur[46] has evaluated efficiencies of wetting agents on wool fabric in respect of performance, structure and cost. Long-chain surface active agents are poorer wetting agents and better detergents than branched-chain materials containing hydrophilic groups in more central structural positions. Of the non-ionic detergents the polyethylene ethers were again found to be particularly effective.

Using sodium bicarbonate and sodium chloride as builders, Morgan and Walter[47] concluded that satisfactory scouring of wool piece goods at low temperatures (80° F.) can be obtained by using larger amounts of detergent than are needed at 120° or 130° F.

Recent work on optical bleaches is described by Landolt.[48] These agents are colourless dyes which produce a bright effect on the fabric by virtue of their capacity to convert ultra-violet light into visible light. The application of these bleaches is limited since the dyes have no cleaning action on the fabric. Those agents presently available are Blankophor

B, R, WT, Tinopol BV, and Uvitex RS, WS. The last named is a recent production and can be used for whitening wool, nylon, silk and acetate rayon.

Dyeing

In the production of level dyeing, Ris, Stocker and Thommen[49] have presented evidence to show that the rate of exhaustion of the dye on to the fibre and the subsequent migrating power of the dye are of prime importance. These properties have been graphed and offer a useful guide to the selection of a suitable method for a particular dyestuff.

In a similar type of study on the levelling properties of acid-dyes Lemin and Ratee[50] found that some sacrifice in exhaustion is necessary to promote levelness. The boil-off can be controlled by increasing the p_H or by addition of levelling agents. Because of the sensitivity of these dyes to p_H change the latter procedure is recommended. Another paper[51] in the series deals with pre-chromed dyes. In this case as the acidity of the dyebath is increased, a maximum is reached in the dyebath exhaustion yielding two p_H values at which exhaustion is equal. Levelling is better at the lower p_H. For the three pre-chromed dyes studied, indications are that boiling off can be done as well with hydrochloric acid as with sulphuric acid, but for any given final p_H, sulphuric acid produces the better boiling off.

Another investigation into the practical aspects of the absorption of acid and chrome dyes by wool has been made by Lister.[52] Relations between dye exhaustion after 5 minutes and p_H and temperature were recorded for various dyestuffs. It was found for example that Glauber's salt retarded the exhaustion of the level dyeing colour, but increased the rate on the intermediate colour. In general, level dyeing colours required a p_H of 4·5–4·7, intermediate colours 5·4–5·7 and unlevel dyeing colours p_H 6–7 for best results. Chromate colours were best dyed at p_H 7–8 and after-chrome colours were similar to acid colours in behaviour.

An investigation[53] has been made to discover why some vat colours are satisfactory for dyeing purposes, but are inferior when used in printing. It was concluded that most vat colours are suitable for both dyeing and printing if the optimum conditions for each colour are found.

Studies have recently been made by Royer, Zimmerman, Walter and Robinson[54] of pressure dyeing at elevated temperatures. Dyeings of wool and wool/cotton unions have been made in less than 90 seconds at 270° F. Tensile properties of the materials are not materially altered. Because of the short time involved, high concentrations of dyestuff must be used for heavy shades, and the p_H of the dyebath must be as high as possible. Satisfactory wool dyeings have been made at p_H 5. A padding technique has been worked out and this renders it practicable to dye continuously at a rapid rate many fabrics which have not previously been dyed continuously. High-temperature dyeing is not so advantageous with cellulosic fibres as with protein fibres. High temperature increases the rate of wool dyeing and brings it closer to that of cotton,and hence is of advantage in union dyeings.

Others[55] working in this field point out similar advantages to be gained from high-temperature dyeing. Maximum safe commercial conditions

for wool were found to be 250° F. at p_H 2·0 for equalizing dyes, p_H 4 for metallized dyes and p_H 6 for milling dyes. In general, 5 minutes at 250° F. gave the same degree of fibre penetration and uniformity of colour as one hour at 212° F. Better results were obtained with 15 minutes at 250° F. It was agreed that by using still higher temperatures under appropriate conditions, continuous practical dyeing might be performed as satisfactorily as the present time-wasting batch methods.

Another laboratory method for the continuous dyeing of wool is described by Casty and Krähenbühl.[56] Wool is first impregnated with dye and then treated in a boiling solution of dilute acid. Level dyeing was obtained in 2–10 minutes with acid dyes and 4–20 minutes with chrome dyes or ester salts of leuco vat dyes and the shade and fastness of the products were similar to normal dyeing. Further industrial developments of this principle will depend upon the design of suitable machines for treating material for a sufficient length of time at a fairly low liquor ratio, with a plentiful flow of liquor through the goods.

Fabrics : miscellaneous

Norman and others[57] have studied the application of spectra to the estimation of resin finishes on textiles. Band emission spectrographs were used to identify both untreated fibres such as wool and nylon and resin-treated fibres. Quantitative measurements of a particular polymer can be made according to the intensity of the band.

Improvements in the water repellency of cotton and wool textile materials have been effected by using 'methyl silicon amine.'[58]

Defects in woollen and worsted cloth fabrics likely to arise out of finishing processes were discussed in detail by Whewell.[59] Among those items discussed were : inadequate setting may be traced to too low temperature or too acid a bath, and damage indicated by loss in weight or poor handle is due to excess alkalinity. Metallic sulphide staining is evident if the crabbing roller is not covered with an adequate length of cotton wrapper. Excessive shrinkage is avoided by using synthetic detergents in the scouring process. Uneven dyeing may be caused by permitting wet alkaline cloth to dry in air. In general, drying should be done at a temperature lower than 180° F. and cloth should be removed from drying as soon as the regain is about 15%. Raising is facilitated by water and wetting agents and care should be taken to avoid reduction in tensile strength. Elsewhere, Whewell and Crawford[60] have shown that treatment of a twill fabric made from 64's quality wool in a 1% solution of Syton retarded the raising of the cloth.

Woolled sheepskins

The main developments in the conversion of sheepskins to resemble natural furs occurred about 1937. During the war tanning methods considerably improved and a new type of fur with trade names, Beaver Lamb, Nutria Lamb and Mouton, was produced. A review of the processes involved is given by Winton.[61] Scouring conditions of the sheepskin are rather critical as the temperature must be kept at a low level to avoid damage to the pelt, whilst this temperature is below the softening points of wool grease and the various fats and waxes in the pelt

itself. The scoured skin is next converted into leather by pickling in acid and salt to condition the collagen before tanning with a reduced chromium sulphate. Liming, beneficial to the pelt, is harmful to the wool fleece and must be omitted. The woolled surface is next degreased and then brushed in a carding machine. The carded woollen surface is sheared to the required fibre length and then ironed in a special machine which produces a decrimped fibre. The tips especially are straightened under the conditions employed. The fleece surface is again shorn and the ironing process repeated several times with 'doping.' The wool now possesses a silky handle and the final conversion to fur may be achieved by a variety of methods, among which are treatments with waxes and aluminium salts or impregnation with formaldehyde, glyoxal or acrolein. Greater permanency is achieved by treatment with U.F. or melamine–formaldehyde resins which are cured during the hot ironing treatment. The finished 'fur' may then be dyed and finally polished.

Miscellaneous

Keggin, Morris and Yuill[71] have measured electrostatic charges on slivers of cotton, viscose, flax, cellulose acetate, wool, casein, Ardil, and nylon, during passage through a cotton flat carding engine. The cellulose fibres tend to be negatively charged whilst the 'protein' type fibres tend to be positively charged. For wool, casein, Ardil, nylon and cellulose acetate, the charge increases with decreasing moisture regain until a steady value is reached. For cotton, flax, and viscose the charge again increases with decreasing regain, but a steady value is not obtained.

Studies such as these are important for the evaluation of new fibres and blends in normal textile processing.

Compounds and methods for mothproofing wool are discussed and a review of the current American anti-shrink wet-chlorination methods for wool are given by Burgess[62] and Spelberg.[63]

Space allows only a very brief mention of the following : recent developments in textile testing and control devices,[64] a series of rapid reproducible methods for the approximate analysis[65] of wool samples at different manufacturing stages, dimensional changes occurring in knitted goods,[66] description of temperature measurement of moving fabrics by radiation pyrometry,[67] an analysis of the physical requirements of clothing suitable for knitted underwear,[68] and the accuracy of various drying procedures for scoured wool.[69] A patent claim is made for the production of permanent fabric finished using an ammonium salt of a styrene–maleic anhydride copolymer simultaneously with a polyamine such as ethylenediamine.[70]

Spinning

The mechanics of the textile processes are outside our present scope, but mention must be made of a new development announced earlier in the year, in the field of worsted spinning.[72] This has been described as the most important spinning advance in the past hundred years. The device is the Ambler Superdraft System and is a system of high speed drafting. 'Drafts of the order obtained render unnecessary approximately two-thirds of the labour and machinery normally used in the preparing

processes of a worsted spinning plant, and so permit the transfer of such operatives displaced to more productive work elsewhere in the mill with a consequent increase in productive machinery capacity.'

Silk

Little new work on silk has been recorded in the literature this year. Tyler [73] gives an account of the development of silk weighting and reviews modern methods. A method which is in general use both in U.S.A. and Europe is described and employs baths of stannic chloride, disodium hydrogen phosphate, sodium silicate and aluminium sulphate. Another review on silk weighting is given by Möller.[74]

A new method for dyeing wool and silk is presented by Mikhailenko[75] *et al.* which produces the dye *in situ* by diazotization of the free NH_2 groups of the keratin or fibroin with subsequent azo coupling. It is claimed that dye fastness is as good as in normal dyeing. This technique provides for a greater variety of shades with wool than with silk.

The moisture regain of silk at 25° C. has been investigated in detail.[76] Comparisons were made of Japanese, Chinese and Italian silks in the gum and after degumming. Identical isotherms were obtained for the first two silks, but Italian silk was found to be slightly more hygroscopic.

Silk fibroin in cupriethylenediamine solution neutralized with acetic acid and dialysed, has been iodinated.[77] Relatively small amounts of thyroxine have been isolated from the iodinated fibroin compared with that obtained from other iodinated proteins. The curtailment of reaction is attributed to steric effects in the silk fibroin molecular structure.

Howitt[78] has reviewed the main points of a discussion at the International Silk Congress at Lyons under the headings: weighting of silk fabrics, suggested yarn-weighting limits, finishing of weighted fabrics for printing, soaking oils, fugitive tints for silk, bleaching, nature of finishing treatment, printing, stabilization and testing of weighted silks, selvedges in silk fabrics, and fastness standards for dyed silk.

Synthetic polypeptides

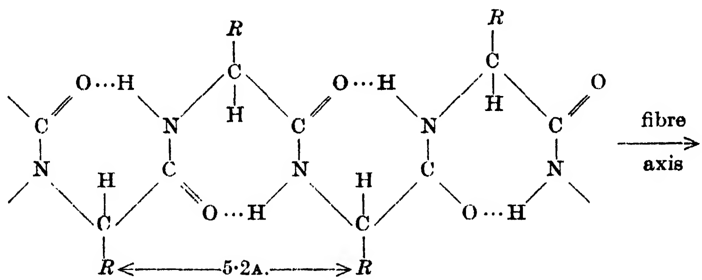
Following the successful syntheses of polypeptides from anhydrides of *N*-carboxy-α-amino-acids by Woodward and Schramm,[82] structural studies have been made on various polymerized amino-acids, notably by Astbury, Dalgleish, Darmon and Sutherland.[83] Pioneering experiments showed a similarity in *X*-ray and infra-red diagrams between synthetic polypeptides and proteins in general. These authors also have evidence for the existence of two types of hydrogen bonds between the CO– and NH– groups of adjacent chains.

Recently Ambrose and Hanby[84] have studied a polyglutamic ester. *N*-carbonic anhydride of γ-methyl-L-glutamate was allowed to polymerize for three months. A film of the polypeptide (from *m*-cresol) was cast on a cadmium sheet and rolled to produce an extension of 500%. The film was still coherent and pliable and showed double refraction. This sample was investigated by polarized infra-red radiation and compared with α-keratin. Indications are that the peptide chains are

folded and maintained in the folded state by intra-chain hydrogen-bonding between the N–H and C=O groups in which the N–H groups tend to lie parallel to the chain axis. A structure involving a 7-membered ring was proposed. (See below.)

Continuing this infra-red work, Ambrose, Elliott and Temple[85] investigated α-keratin (porcupine quill), β-keratin (swan quill), myosin and tropomyosin. All spectra showed two bands which arise from the N–H stretching modes. Both bands show parallel dichroism in myosin, tropomyosin and α-keratin, but are markedly perpendicular in β-keratin and it is assumed that the same backbone is present in these alpha-proteins as in the polyglutamic ester.

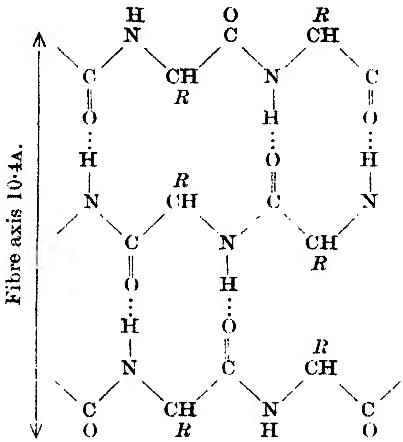
X-ray studies of fibres spun from : (*a*) a copolymer of L-glutamic γ-methyl ester with DL-β-phenylalanine, and (*b*) a poly-DL-β-phenylalanine were made by Bamford, Hanby and Happey.[86] In (*a*) the repeat distance is 5·26 A., along the fibre axis and in (*b*) the repeat distance is 5·28 A., and it is suggested that an α-fold is present containing two amino-acid residues in the repeat distance. Although the fibres have been oriented, no β-configuration was noted. The *X*-ray data agree with the structure postulated by Ambrose and Hanby above.



These authors maintain that the results of Brown, Coleman and Farthing (below) could be explained without assuming that the chains lie perpendicular to the fibre axis and without postulating a 'backbone spacing' of 4·65 A. as a repeat of 5·2 A. along the fibre axis.

Brown, Coleman and Farthing[87] have confirmed the *X*-ray work of Astbury and Dalgleish above in synthetic polypeptides in that most of them resemble the β-protein structure. However, copolymers of DL-β-phenylalanine and L-leucine, and of DL-β-phenylalanine, and α-amino-*iso*butyric acid yield *X*-ray powder photographs whose two principal diffraction rings correspond to interplanar spacings of 5·2 and 11·7 A. Films of these copolymers yield an oriented diffraction pattern similar to those of α-proteins. Fibres spun from the phenylalanine–leucine copolymer yield fibre photographs of a character so similar to natural keratin that it is believed they are produced by the same type of molecular configuration. It has not yet been possible to extend the synthetic fibres into the β-configuration. Evidence suggests that the polypeptide chains in both natural and synthetic α-keratin fibres do not

lie parallel to the length of the fibre, but transverse to it. That is, the structure is held together along the fibre by hydrogen bond systems and by side chain interlocking. This interesting hypothesis is being further investigated.



Criticisms of the above *X*-ray work have been offered by Astbury[88] who is not yet satisfied that sufficient proof has been obtained to support the α-diagram or the correctness of the α-fold of these synthetic polypeptides. He rejects the type of fold advocated by Ambrose *et al.* since it would not give a strong meridional reflexion at about 5·1 A. and he maintains that considering all sources of evidence the 5·1A. reflexion is associated with a repeat of three amino-acid residues, not two. Astbury maintains that the suggestion of Brown *et al.* that the 5·2 A. spacing is the orthodox backbone spacing between extended polypeptide chains is untenable since the latter is usually about 4·65 A. in fibrous β-proteins and cannot exceed[89] about 4·77 A. It is of interest to note that Bamford *et al.* found the supposed α-diagram with fibres of poly-DL-phenylalanine whereas Astbury *et al.* working with a powder preparation found a β-diagram. Thus, further investigation of this synthetic polypeptide might settle the question if one of the two forms is really α.

Darmon and Sutherland[90] also draw attention to the fact that much groundwork remains to be done on the infra-red spectrographic investigation of proteins and synthetic polypeptides. In particular, the existence of the two bands in the region between 3000 cm.$^{-1}$ and 3400 cm.$^{-1}$ attributed to NH ······ CO bonds require considerably more work to help elucidate the structure of these polypeptides.

Klötz, Griswold and Gruen[91] have recently reported on infra-red absorption spectra for a series of polypeptides and for the complexes of these substances with sodium dodecyl sulphate. The spectra of the latter indicate that the dodecyl sulphate perturbs more than one group in the protein.

Regenerated protein fibres

Interest is still pronounced in the field of protein synthetic fibres and the attractive idea of rendering the globular protein molecule into the fibrous form is being pursued. Methods for insolubilizing and stabilizing these fibres depend mainly upon the formation of what are probably methylene and methylene ether links between the polypeptide side chains by means of formaldehyde. The reaction of proteins with formaldehyde is not yet completely understood despite the existence of quite an extensive literature on the subject. A useful review of this reaction has recently been made by Traill.[92] Osmotic pressure measurements on proteins containing amino groups previously treated with formaldehyde at p_H 3 to 8 have been shown by Fraenkel-Conrat and Mecham[93] to indicate an increase in molecular weight of the treated protein. This is probably due to the linking up of two or more protein molecules by means of methylene bridges between the amino and other reactive groups. Amide groups do not readily react under these conditions, but it is generally concluded that in highly acid conditions the amide groups play a part in the cross-linking reaction. Middlebrook[94] has examined the reaction of formaldehyde with wool, among other proteins, under acid conditions. He concludes that the formaldehyde forms cross linkages between the glutamic amide groups and possibly the guanidyl groups of arginine. These cross linkages can be broken down by distillation in dilute phosphoric acid. A theory is advanced that formaldehyde also combines with asparagine amide groups to form 6-hydroxytetrahydropyrimidine 4-carboxylic acid which is stable to boiling dilute phosphoric acid.

The action of formaldehyde on zein fibres has been studied by Evans and Croston[95] and is mentioned below.

The strengths of protein synthetic fibres are lower than wool, but improvement is expected to come by novel methods of 'denaturation' of the globular molecule or by more efficient cross linkages. Much more investigation is required of the molecular shape as distinct from the molecular weight of protein suitable for spinning purposes.

Boyd and Eberl[96] have postulated a chain mechanism for the denaturation of tobacco mosaic virus and other proteins. This has been deduced from studies of the absolute reaction rate theory as applied to the denaturation phenomenon and accounts for many of the experimental data. Free energies and entropies and heats of activation have also been calculated.

Among the fundamental requirements for protein fibre formation are long molecular chain length and molecular alignment. In attempts to produce a less degraded protein molecule than is obtained from highly alkaline spinning solutions, work has been directed in recent years to the use of protein-detergent complexes. Lundgren[97] and Senti[98] have investigated these in detail. In some cases, particularly with egg albumen, fibres exhibiting high degree of orientation and high tensile strengths have been obtained.

A recent patent[99] describes the production of fibres based on casein, using 16 parts casein in a solution of 8 parts of sodium dodecyl sulphate

in 76 parts water for 18 hours at p_H 5·8. The protein fibres are spun into liquor containing sodium sulphate, sulphuric acid, glucose and aluminium sulphate and finally hardened with formaldehyde. Another patent[100] claims the production of filaments by spinning an alcoholic solution of a complex formed between casein or other proteins and sodium dodecyl sulphate. It does not appear however that a satisfactory process of this type has yet been established to give fibre strengths greater than normal.

Recently, investigations have been made into methods for dispersing keratin, particularly wool, in a condition suitable for regenerating a protein fibre. For example, Jones and Mecham[101] suggest dissolving wool in a neutral aqueous solution of a sulphur-containing reductive disulphide-splitting agent such as monoethylene thioglycol or ammonium cyanate. Other patents claim similar compounds including calcium thioglycollate and thiosorbitol. It is claimed that regenerated wool fibres of 80% normal strength may be obtained by these methods.

Wormell[102] has spun filaments from a blend of casein and a wool degradation product. The latter was obtained by dissolving wool in sodium sulphide solution and precipitating with dilute hydrochloric acid. The blend was spun from a caustic soda solution into a bath of sodium and magnesium sulphates in acid solution. The tensile strengths of the blended fibres are lower than 100% casein. Later, Wormell and Happey[103] have dissolved soluble keratin curd in dilute cuprammonium solution and precipitated with sulphuric acid. After water washing this was repeated and the solution spun into a sulphate bath at p_H 7·0 containing 0·1% 'Fixanol.' The resulting fibre was hardened in formaldehyde. X-ray photographs show the β-keratin or fully-extended form and no evidence of the α-fold of the original wool molecule.

Mercer,[104] however, in an interesting investigation has reported on the production of a regenerated wool fibre showing an α-type X-ray pattern. The major fraction of wool keratin was dissolved in saturated urea solution containing reducing agents. The dissolved protein was salted out and two forms were found to occur. One form could be drawn out into fine fibres with marked birefringence and showing the original α-type X-ray pattern. Preliminary ultra-centrifugal measurements show that the dissolved keratin is polydisperse and has a much greater molecule weight than dispersions in reducing agents at a high p_H, such as sodium sulphide.

From investigations of this type much useful information should be gained of the conditions for protein fibre formation.

Happey[142] has advanced two hypotheses for Mercer's α-keratin structure in regenerated wool fibre. The first is based on highly oriented casein fibres and the second on the results of Bamford and co-workers[86] that certain polypeptides apparently fold in the α-form.

Brief mention of recent advances reported on specific protein fibres is given below.

Groundnut protein fibre

It has been announced that 'Ardil,' a fibre made from groundnut protein, will be manufactured in this country within the next two years.

A patent specification[105] claims the treatment of coagulated groundnut-protein filaments with a 3–4 molar solution of an alkali sulphate containing formaldehyde and sulphuric acid so that the p_H is $<0{\cdot}5$. This yields insolubilized fibres which are resistant to acid dye liquors. Another patent[106] claims the addition of small amounts of potassium cyanide to a spinning solution of groundnut protein to stabilize the viscosity and prevent skin formation.

Casein fibres

Spinning solutions obtained by the Todtenhaupt-Ferretti process were based on 'textile' casein, i.e. casein precipitated under specific conditions from skimmed milk by means of sulphuric acid.

Winkler[107] describes the addition of oxalic acid and thioglycollic acid or sodium sulphide to alkaline solutions of rennet casein. These 'improve' the protein, and filaments as good as those from 'textile' casein can be obtained. The oxalic acid splits off inorganic materials and the solubility is increased by the albumen solvents, thioglycollic acid or sodium sulphide.

Peterson, McDowell and Hoover[108] have described a process for spinning continuous filament casein yarn. Casein is dissolved in caustic soda to give a 25% solution at p_H 7·0 and extruded into an acetic acid bath. The tow is then stretched 100% in an aluminium sulphate–formaldehyde bath and treated in a p_H 6·0 sodium acetate bath. The casein yarn is then collected in a centrifugal pot, stoved, washed and dried in cake form and finally acetylated. The fibre has a tensile strength of 1·0–1·2 g per denier. It is said that the process does not give complete stabilization but the fibre withstands acid dye treatment for 1 hour at 80° c.

The production of a new casein fibre, 'Caslen,' has been announced.[109] It is produced as monofilaments or coarse staple of 195–1330 denier. The tenacity is reported to be 0·8–1·0 g. per denier. The process consists essentially of coagulating, stretch, hardening, washing and drying. Present experimental uses for staple 'Caslen' are as a blend with wool for making filter felt and to replace hair in mattresses.

Zein

Interest in the protein synthetic-fibre field in America has partially switched to zein, a protein derived from maize.[110] It will be recalled that Croston *et al.*[110] described the development of a practical process for the production of zein fibres. Non-tacky, high-viscosity solutions of 13–16·5% zein in water, caustic soda, urea and formaldehyde were used for spinning. After coagulation in a sulphuric/acetic acid bath containing zinc sulphate the fibres were pre-cured in formaldehyde, rinsed, stretched and dried at 65° c. Evans and Croston[95] have developed a practical method for curing zein fibres and studied the reaction mechanism. Because zein has a different amino-acid composition and fewer reactive groups than other proteins, the reaction with formaldehyde is also different. In the production of zein fibres, a pre-cure is given in a bath containing 10% formaldehyde, 1% ammonium sulphate, 5% sodium sulphate at p_H 2·4. The object of this pre-cure is to produce a high

strength fibre to withstand acetylation. Post-cure is applied to stretched and oriented fibres to insolubilize the product. A low p_H is preferred, when the formaldehyde is bound irreversibly and control of shrinkage attained.

In the earlier part of this year the commercial production of a new zein fibre 'Vicara' was announced in U.S.A.[111] This protein fibre undoubtedly is superior to any other previous American commercial protein fibre. The production of the fibre involves a partial curing of the coagulated tow, stretching and final curing. 'Vicara' possesses a resilient handle, high modulus of elasticity at low elongations, high work recovery and good scouring and laundering properties due to its very great alkaline resistance. 'Vicara' is cream coloured and has a dry tenacity of 1·0 g. per denier and a wet tenacity of 0·5 g. per denier, a dry elongation at break of 42% and a wet elongation at break of 50%. Because of its high acid and alkali resistance, 'Vicara' can be carbonized, mercerized and dyed at high temperatures. It is claimed that the fibre processes admirably in the usual textile machinery and among end-uses mentioned are women's dress goods, suitings, knit goods, hosiery and upholstery, etc.

Cotton-seed protein

The difficulty of gelation in alkaline dispersions of cotton seed meal protein is overcome by treating the extracted protein with an aqueous acid solution.[112] Clear non-gelling solutions in alkali may then be prepared and spun in the normal manner to form filaments which may be hardened and dried by the normal procedures.

Nylon

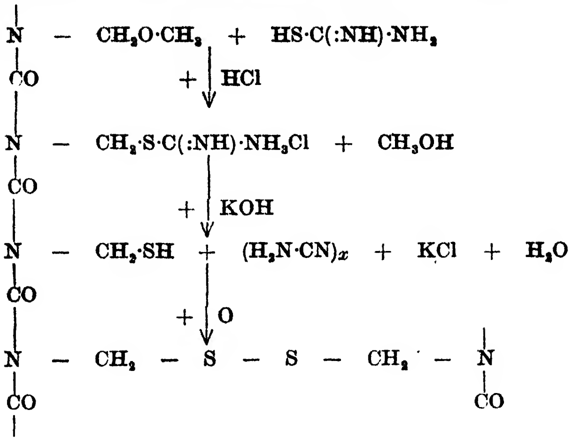
Elastic nylon

Cairns and others[113] have treated linear polyamides with formaldehyde under various conditions to produce N-hydroxymethyl-, N-alkoxymethyl- and N-alkylthiomethyl-polyamides. As the degree of substitution increases, the m.p. and the fibre tensile strength decrease. Elastic recovery from stretching is greatly increased and in some cases a rapid recovery of 90–95% is obtained from an elongation up to 500%.

If the alkoxymethylpolyamides are heated[114] with aqueous acid, the substituent group is hydrolysed off and the amide group is regenerated. If, however, it is heated in absence of water in presence of acid, interchain condensation occurs thus:—

$$\begin{array}{lclcl} | & & | & & | \qquad\qquad\qquad | \\ N{-}CH_2{\cdot}O{\cdot}CH_3 & + & NH & \xrightarrow{H^+} & N{-}CH_2{-}N \quad + \quad CH_3OH \\ | & & | & & | \qquad\qquad\qquad | \\ CO & & CO & & CO \qquad\qquad\quad CO \\ | & & | & & | \qquad\qquad\qquad | \end{array}$$

A method is described of preparing high polymers with a controllable number of cross links between the chains, by the action of thiourea on N-methoxymethyl-'66' nylon :—



Wittbecker[115] *et al.* have also shown that by using secondary diamines instead of primary amines, the property of rubberiness may be imparted to the *N*-methylpolyamide fibres produced.

A number of patents[116] on the reaction of polyamides with formaldehyde and with other reagents are available.

Hill and Walker[117] give a comprehensive review of the relationship between chemical structure and the fibre-forming properties of a large number of linear condensation polymers including amides, esters and urethanes. Ether and ester links lower the m.p. whilst $\cdot NH\cdot CO_2\cdot$, $\cdot CO\cdot NH\cdot$ and $\cdot NH\cdot CO\cdot NH\cdot$ links, in that order, raise the m.p. owing to lateral attraction between polar groups. This study is fundamental to future modifications of fibres from condensation polymers, especially with regard to physical properties, such as dyeing, which can be partly correlated with the chemical structure of the polymer.

Additional determinations of moisture regain have been made for '66' nylon.[118] Further data[119] on the moisture absorption of nylon shows that wetting in water produces an irreversible change in moisture absorption, especially in drawn nylon. In quantitative determinations[120] of nylon in nylon–wool blends, potassium hydroxide is used to dissolve out the wool and for nylon–acetate blends, acetone is used to remove the cellulose acetate.

Dyeing

So far, the most satisfactory dyes available for nylon[121] are the cellulose acetate rayon dyes which are mostly fine dispersions of insoluble materials. These become spread over the fibre surface and then are absorbed into the nylon to form a solid solution. Although a wide variety of shades may be obtained not all are fast to light and washing. Acid wool dyes on nylon at low p_H give an extended range of shades with good fastness to light and washing. Direct cotton dyes are not so fast to light but from both these types of dye really deep shades are not readily obtainable. The light fastness of vat dyes on nylon is poor. Chrome dyes which

yield the greatest fastness to light and washing on wool can also be used for nylon, but unfortunately tend to produce tendering of the nylon fibre. Research is at present active on the problems of nylon dyeing.

Egerton[122] presents additional results on the photochemical degradation of cellulose acetate rayon and nylon yarns dyed with dispersed and soluble acetate dyes. Many of the dyes degraded nylon to a much greater extent than cellulose acetate rayon as measured by tensile strength after light exposure. Dyes which increase the effect on nylon, which has been traced to an oxidation process, are least fast to light on this fibre.

Detailed results of fastness tests for acid, chromacyl and chrome dyes on nylon are given in a du Pont technical bulletin.[123] Chromacyl dyes have good fastness to acid perspiration and sea-water immersion and chrome dyes to acid and alkaline perspiration, but both types of dyes exhibit poor fastness to peroxide bleaching.

Methods of dyeing nylon with chrome dyes are critically discussed by Hadfield and Sharing.[124] From a study of the absorption of potassium dichromate by plain and dyed nylon, it appears that the groups in nylon responsible for the absorption of the dye are also concerned with the absorption of the dichromate ions.

Suitable dyes for Perlon are discussed in detail and classified according to chemical properties.[125] The absorption of acid and substantive dyes by Perlon, Perlon L and nylon are also discussed in another paper.[126]

Terylene

The early development of 'Terylene,' the fibre formed from the polyester polyethylene terephthalate, is discussed by Hardy.[127] The preparation of raw materials, polyester and the production of continuous filaments are described and the properties of the fibre listed. The ester linkages are more stable to heat and light than the amide linkages in fibroin or in the polyamides, hence 'Terylene' has excellent resistance to heat, light, acids, solvents and bleaching agents. 'Terylene' may be heat-set like nylon and possesses good resilience and strength characteristics, but like nylon does not dye readily.

A large number of patents on 'Terylene' and allied polymers have recently been disclosed. These relate largely to details in processing and space does not permit a full account. Topics such as the recovery of terephthalic acid from scrap polymer,[128] the production of patterned effects on dyeing together stretched and unstretched 'Terylene,'[129] the production of high molecular weight filaments by heating dry polymer in absence of oxygen, are covered.[130] Other claims include the strengthening of filaments by cold[131] or hot drawing,[132] the latter of which is facilitated by wetting in water or dilute glycerol.[133]

Other patents disclose interesting variations on 'Terylene,' such as the preparation of linear polyesters to form filaments of higher m.p. and lower solubilities than 'Terylene' by treating a naphthalenedicarboxylic acid with a glycol.[134] Another series of linear polyesters is obtained from acids of the general formula $R[C_6H_4(COOH)_2]_2$ where R is O, $-OCH_2-$, $-OCH_2{\cdot}C_6H_4{\cdot}CH_2O-$ or $-O{\cdot}C_6H_4O-$. The preparation of linear

polyesters by self-polymerization of hydroxy-carboxylic acids such as $HO{\cdot}R{\cdot}C_6H_4{\cdot}COOH$ where R is $(CH_2)_{1 \text{ or } 2}$ or $-O-(CH_2)_{1,2 \text{ or } 3}$ is also covered by patent[135]. Doubtless time will elapse before these products are publicly evaluated as textile fibres.

Polyacrylonitrile fibres

Research on polyacrylonitrile fibres in Germany[136] received a stimulus on the appearance of nylon and Perlon and the large-scale production of acrylonitrile from acetylene and hydrocyanic acid at I.G. Farben, Leverkusen. Search was made for a suitable spinning solvent and lactams, lactones, formylized primary and secondary amines, sulphones, etc. were found to be promising.

In 1948, du Pont in U.S.A. announced the production of 'Orlon,' a 100% polyacrylonitrile fibre, on a pilot-plant scale. Dimethylformamide is used principally as the solvent for dry spinning.[137] Wet spinning may also take place in a hot 20% solution in dimethylformamide coagulated in hot glycerol. 'Orlon' has tensile properties approaching nylon. The flex life and resistance to outdoor exposure is outstandingly good and it gives satisfactory performance over a wide temperature range. Difficulty in dyeing constitutes the main disadvantage of 'Orlon' at present, but latest statements from du Pont say that deep, bright colours of wash fastness have been obtained in laboratory experiments.

Details of the chemical researches which led up to the development of Vinyon N fibres, the production process and the characteristic properties of the various stretched types are described by Hall[138] in a general article. Further details[139] disclose that Vinyon N, which is a copolymer of vinyl chloride and acrylonitrile, may be either dry-spun or wet-spun from a solution in acetone. The former process is used to produce[140] continuous filament while the wet process is used for the production of staple and heavy-denier yarn. It is reckoned that Vinyon N yarns will find application in drapery and upholstery fabrics in addition to other special textile applications.

Recent patents,[141] irrelevant to this section, but of some importance, disclose the interesting achievement in the production of fibres from rubber or synthetic polymers of dienes by reaction with SO_2 in presence of organic or inorganic hydroperoxides. Research and development on this line may in time lead to a completely new set of fibres possessing novel textile characteristics.

References

1 Frishman, D., *et al.*, *Ind. Eng. Chem.*, 1948, **40**, 2280
2 Farnworth, A. J. and Speakman, J. B., *Nature*, 1949, **163**, 798
3 Farnworth, A. J., Neish, W. J. P. and Speakman, J. B., *J. Soc. Dy. Col.*, 1949, **65**, 447
4 Farnworth, A. J. and Speakman, J. B., ibid., April, 1949
5 Alexander, P., Carter, D. and Hudson, R. F., ibid.
6 Wolsey, Ltd. and Alexander, P., B.P. 613,267
7 Alexander, P., Carter, D. and Earland, C., *J. Soc. Dy. Col.*, March 1949
8 Wolsey Ltd. and Alexander, P., B.P. 611,828–9
9 Lipson, M. and Speakman, J. B., *J. Soc. Dy. Col.*, 1949, **65**, 390
10 Capp, C. W. and Speakman, J. B., ibid., 402

[11] L. A. Fluck, *Amer. Wool & Cotton Reptr.*, 1949, **63**, 13
[12] Stock, C. R. and Salley, D. J., *Text. Res. J.*, 1949, **29**, 41
[13] British Cotton and Wool Dyers' Assoc. Ltd., B.P. 614,966
[14] Wolsey, Ltd. and Alexander, P., B.P. 618,794
[15] Speakman, J. B., Crummett and British Celanese Ltd., B.P. 609,370
[16] Wolsey Ltd., *et al.*, B.P. 611,360
[17] Rust, J. B. and Montclair Research Corpn., U.S.P. 2,447,538–539–540–772–876 877–878, 2,448,004–5
[18] B.P. 612,154
[19] B.P. 615,473
[20] G. H. Michell & Sons Ltd., Australian Pat. 128,039
[21] Palestine Potash Ltd., B.P. 614,271
[22] U.S.P. 2,457,033
[23] Milton Harris Associates, B.P. 621,989, 609,370
[24] Speakman, J. B., *J. Text. Inst., Manchr.*, 1947, **38**, T102
[25] Idem, *Nature*, 1948, **161**, 890
[26] Blackburn, S. and Lindley, H., *J. Soc. Dy. Col.*, 1948, **64**, 305
[27] Cockburn, R., Drucker, B. and Lindley, H., *Biochem. J.*, 1948, **43**, 438
[28] Elöd, E. and Zahn, H., *Kolloid Z.*, 1944, **108**, 94; Zahn, H., *Z. Naturforsch.*, 1947, **26**, 286
[29] Idem, *Textilber.*, 1947, **28**, 2
[30] Idem, ibid., 1949, **30**, 17
[31] Alexander, P., *Research*, 1949, 246
[32] Peters, L. and Speakman, J. B., *J. Soc. Dy. Col.*, 1949, **65**, 63
[33] Kitchener, J. A. and Alexander, P., ibid., 284
[34] Peters, L. and Speakman, J. B., ibid., 285
[35] Kirst, W., *Textilber.*, 1947, **28**, 169
[36] Idem, ibid., 314
[37] Idem, ibid., 394
[38] Elöd, E. and Zahn, H., ibid., 1948, **29**, 17
[39] Kirst, W., ibid., 236
[40] Stoves, J. L., *Nature*, 1946, **157**, 230; Stoves, J. L., *J. Soc. Leath. Tr. Chem.*, 1948, **32**, 254
[41] Blackburn, S., *Biochem. J.*, 1948, **43**, 114
[42] Lindberg, J. and Gralen, N., *Text. Res. J.*, 1949, **19**, 183
[43] Leonard, E. A. and Winch, A. R., *Rayon synth. Text.*, 1949, **30**, 79, 93
[44] Leonard, E. A., and Beck, L., *Amer. Dyes. Reptr.*, 1949, **38**, 348
[45] Dobozy, K. O., *Industr. Text.*, 1948, **65**, 297
[46] La Fleur, K. S., *Amer. Dyes. Reptr.*, 1949, **38**, 367
[47] Morgan, O. M. and Walter, J. E., ibid., 374
[48] Landolt, A., ibid., 353
[49] Ris, H., Stocker, W. and Thommen, E. W., *J. Soc. Dy. Col.*, 1948, **65**, 297
[50] Lemin, D. R. and Ratee, I. D., ibid., 1949, **65**, 217
[51] Idem, ibid., 221
[52] Lister, C. H., ibid., 97
[53] Amer. Assoc. Text. Chemists and Colorists, Rhode Island Section, *Amer. Dyes. Reptr.*, 1949, **38**, 69
[54] Royer, G. L., Zimmerman, C. L., Walter, H. J., Robinson, R. D., *Text. Res. J.*, 1948, **18**, 598
[55] Amer. Assoc. Text. Chemists and Colorists, Philad. Section, *Amer. Dyes. Reptr.*, 1949, **38**, 9
[56] Casty, R. and Krähenbühl, E., *J. Soc. Dy. Col.*, 1949, **65**, 381
[57] Norman, D. P., Johnson, W. W. A. and Johnson, N. S., *Amer. Dyes. Reptr.*, 1948, **37**, 838
[58] Meakins, R. J., *J. Coun. sci. Industr. Res. Aust.*, 1948, **21**, 222
[59] Whewell, C. S., *J. Soc. Dy. Col.*, 1949, **65**, 9
[60] Whewell, C. S. and Crawford, J. B., *J. Text. Inst.*, 1949, **40**, T341
[61] Winton, E. R., *J. Soc. Dy. Col.*, 1949, p. 333
[62] Burgess, R., *J. Soc. chem. Ind.*, 1949, **68**, 121
[63] Spelberg, J., *Amer. Dyes. Reptr.*, 1949, **38**, 526
[64] Davis, L. J., *Text. Recorder*, 1949, **66**, 52
[65] Van Overbeke, M. and Mezingue, G., *Int. Wool Text. Org.*, 1948, **2**, 68

[66] Fletcher, H. M., Duensing, M. E. and Gilliam, J. F., *Amer. Dyes. Reptr.*, 1949, **38**, 481
[67] Bowden, C. W., *Text Res. J.*, 1949, **19**, 342
[68] Cassie, A. B. D., *J. Text. Inst., Manchr.*, 1949, **40**, P144
[69] LeCompte, G. C. and Lipp, H. H., *Amer. Dyes. Reptr.*, 1949, **38**, 484, 512
[70] Powers, D. H., Rossin, E. H. and Monsanto Chemical Co., U.S.P. 2,469,407–8–9
[71] Keggin, J. F., Morris, G. and Yuill, A. M., *J. Text. Inst., Manchr.*, 1949, **40**, T702
[72] *Wool Digest*, May 1949 ; *Text. Wkly*, 1949, **43**, 1090, May 13
[73] Tyler, A. G., *Dyer*, 1949, **101**, 429
[74] Möller, E., *Kunstseide u. Zellwolle*, 1949, **27**, 98
[75] Mikhailenko, P. I., *et al.*, *Chem. Abstr.*, Aug. 10, 1948, **42**, 5676F
[76] Hutton, E. A. and Gartside, J., *J. Text. Inst., Manchr.*, 1949, **40**, T161
[77] Michel, R. and Pitt Rivers, R., *Biochim. Biophys. Acta*, 1948, **2**, 223
[78] Howitt, F. O., *Dyer*, 1948, **100**, 189
[79] Lindberg, J. and Gralen, N., *Text. Res. J.*, 1948, **18**, 287 ; ibid., 1949, **19**, 98 ; ibid., 1949, **19**, 183 ; Lindberg, J., ibid., 1948, **18**, 470
[80] Makinson, K. R., *Trans. Faraday Soc.*, 1948, **44**, 279 ; *Text. Res. J.*, 1949, **19**, 97
[81] Frishman, D., Smith, A. L. and Harris, M., ibid., 1948, **18**, 475
[82] Woodward and Schramm, *J. Amer. chem. Soc.*, 1947, **69**, 1551
[83] Astbury, W. T., Dalgleish, G. E., Darmon, S. E. and Sutherland, G. B. B. M., *Nature*, 1948, **162**, 596
[84] Ambrose, E. J. and Hanby, W. E., ibid., 1949, **163**, 483
[85] Ambrose, E. J., Elliot, A. and Temple, R. B., ibid., 859
[86] Bamford, C. H., Hanby, W. E. and Happey, F., ibid., **164**, 138
[87] Brown, C. J., Coleman, D. and Farthing, A. C., ibid., **163**, 834
[88] Astbury, W. T., ibid., **164**, 439
[89] Idem, ibid., **163**, 722
[90] Darmon, S. E. and Sutherland, G. B. B. M., ibid., **164**, 440
[91] Klötz, Griswold and Gruen, *J. Amer. chem. Soc.*, 1949, **71**, 1615
[92] Traill, D., *Chem. & Ind.*, 1950, 23
[93] Fraenkel-Conrat, H. and Mecham, D. K., *J. biol. Chem.*, 1949, **177**, 477
[94] Middlebrook, W. R., *Biochem. J.*, 1949, **44**, 17
[95] Evans, C. D. and Croston, C. B., *Text. Res. J.*, 1949, **19**, 202
[96] Boyd, G. A. and Eberl, J. J., *J. phys. Colloid Chem.*, 1948, **52**, 1146
[97] Lundgren, H. P., *Silk J. & Rayon World*, 1946, **23**, 40 ; Lundgren, H. P. and O'Connell, *Ind. Eng. Chem.*, 1944, **36**, 370
[98] Senti, Copley and Nutting, *J. phys. Chem.*, 1944, **49**, 192
[99] Watson, F. K. and E. I. duPont, U.S.P. 2,403,251
[100] Dimsdale, W. H. and Smith, R. C. M. and Ilford Ltd., B.P. 610,647
[101] Jones, C. B. and Mecham, D. K. and U.S. Secretary of Agriculture, U.S.P. 2,445,029
[102] Wormell, R. L., *J. Text. Inst., Manchr.*, 1948, **39**, T219
[103] Wormell, R. L. and Happey, F., *Nature*, 1949, **163**, 18
[104] Mercer, E. H., ibid., 18
[105] Traill, D. and McLean, A. and I.C.I. Ltd., B.P. 605,830
[106] Millidge, A. F. and Knight, C. L. and Courtaulds Ltd., U.S.P. 2,459,952
[107] Winkler, W., *Kuntseide u. Zellwolle*, 1948, **26**, 66
[108] Peterson, R. F., McDowell, R. L. and Hoover, S. R., *Text. Res. J.*, 1948, **18**, 744
[109] Bendigo, C. W., *Text. World*, 1949, **99**, 106
[110] Croston, C. B., Evans, C. D. and Smith, A. K., *Ind. Eng. Chem.*, 1945, **37**, 1194
[111] Ter Horst, W. P., *Amer. Dyes. Reptr.*, 1949, **38**, 335
[112] U.S.P. 2,642,933
[113] Cairns, T. L., Foster, H. D., Larcher, A. W., Schneider, A. K. and Schreiber, R. S., *J. Amer. chem. Soc.*, 1949, **71**, 651 ; B.P. 608,335
[114] Cairns, T. L., Gray, H. W., Schneider, A. K., Schreiber, R. S., ibid., 655
[115] Wittbecker, E. L., Hontz, R. C., Watkins, W. W., *Ind. Eng. Chem.*, 1948, **40**, 875
[116] U.S.P. 2,430,859, 2,430,860, 2,430,867, 2,430,875, 2,430,907, 2,430,908, 2,430,910, 2,430,923, 2,430,953, 2,434,247, 2,439,745, 2,441,085, 2,443,486, 2,459,831, 2,462,430
[117] Hill, R. and Walker, E. E., *J. Polymer Sci.*, 1948, **3**, 609
[118] Hutton, E. A. and Gartside, J., *J. Text. Inst., Manchr.*, 1949, **40**, T170
[119] Abbott, J. N. and Goodings, A. C., ibid., T232

[120] Bennett, R. D., *Canad. Textile J.*, 1949, **66**, 71
[121] *Text. Wkly*, 1949, p. 450
[122] Egerton, G. S., *J. Soc. Dy. Col.*, 1948, **64**, 336
[123] E. I. du Pont de Nemours & Co. Bull., 1948, **4**, 121, 175
[124] Hadfield, H. R. and Sharing, D. N., *J. Soc. Dy. Col.*, 1948, **64**, 381
[125] Müller, J., *Textilber.*, 1949, **30**, 106, 147, 199
[126] Elöd, E. and Fröhlich, G., ibid., 103
[127] Hardy, D. V. W., *J. Soc. chem. Ind.*, 1948, **67**, 426
[128] Heath, R. L. and I.C.I., Ltd., B.P. 610,135
[129] Vickerstaff, T. and I.C.I. Ltd., B.P. 609,946
[130] Byers, J. S., Swallow, J. C. and I.C.I. Ltd., B.P. 609,796
[131] Whinfield, J. R. and Dickson, J. T., B.P. 603,827
[132] Leben, L., Little, A. H. and I.C.I., Ltd., B.P. 603,840, Little, A. H. and I.C.I. Ltd., B.P. 603,838
[133] Reynolds, R. J. W., Wood, L. and I.C.I. Ltd., B.P. 603,842
[134] Cook, J. G., Huggill, H. P. W., Lowe, A. R. and I.C.I. Ltd., B.P. 604,073
[135] Cook, J. G., Dickson, J. T., Lowe, A. R. and Whinfield, J. R., B.P. 604,985
[136] Rein, H., *Z. angew. Chem.*, 1948, A60, 159
[137] Quig, J. B., Papers Amer. Assoc., *Textile Tech.*, 1949, **4**, 61
[138] Hall, A. J., *Silk & Rayon*, 1949, **23**, 118
[139] Rugeley, E. W., Field, T. A. and Freman, G. H., *Ind. Eng. Chem.*, 1948, **40**, 1724
[140] Glenn R. D., Kernan, J. R. and Swalen, G. M., *Chem. Engng. Progr.*, 1949, **45**, 180
[141] N.V. de Bataafsche Petroleum Maatschappy, B.P. 500,515, 527,075, 611,919, 616,276
[142] Happey, F., *Nature*, 1949, **164**, 184

LEATHER AND GLUE

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DURING the year under review, no outstanding advances have been made in the field covered. On the other hand, developments have taken place along a number of lines with which leather chemists are already familiar, and in addition, noteworthy attempts have been made to apply modern optical and electrometric methods to research and analytical control. Although some of these are still in the experimental stage, results so far are encouraging and no doubt it will be possible to report at a later date their widening application. Attention is being turned increasingly to the utilization of synthetic materials, especially for tanning, where uncertainties regarding future supplies of natural products lends urgency to the problem. In this connexion, it is not surprising to see several reports on the use of synthetic resins as tanning agents, and there is no doubt that chemists will have to explore many kinds of substitute which can be manufactured and used economically.

Since most of the reactions taking place during the making of leather are between complex bodies, it is only natural that there should be controversy regarding some of them. In all cases, however, the main reactions which take place are known, but there is ample scope to examine them more fully. Of these the most important are the vegetable and chrome tanning reactions; a great deal of attention is being paid in vegetable tanning to methods for estimating accurately the constituents of tanning liquors, since until this is done there is little use in drawing definite conclusions as to their behaviour. In the field of chrome tanning contributions have been fewer than usual; much of the reported work is on the behaviour of chromium salt solutions.

Few communications on glue and gelatin have been noted, nor has a great deal of attention been paid to those operations which precede tanning in the normal course of manufacture.

Animal skin proteins

As hides and skins of animals are the tanner's principal raw materials, contributions to our knowledge of skin proteins in general and collagen in particular are of special interest to the leather chemist. Several investigators have published papers worthy of note during the year under review, and all tend to emphasize the complexity of this field of study. Dempsey and Garrod[1] point out that results obtained in experiments carried out on collagen from rat-tail tendon would not necessarily correspond to results using collagen from other parts of the skin, since collagen varies in composition depending on the source. The binding sheath in tendon is different from that in skin; its importance to the tanner is emphasized,

especially in the influence it has in the swelling and plumping of pelt in the depilating operations. Turner[2] traces the relationship between such factors as breed, nutrition, age and climatic conditions, and skin quality.

A method for determining the protein fractions of animal skins has been proposed by Jacobs[3]: (i) The protein is digested in 0·1% HCl for one hour at 85° c. and the elastin and keratin removed by filtration. (ii) Globular proteins in the filtrate are precipitated by 3% trichloracetic acid; total proteins in the same filtrate are precipitated by 30% trichloracetic acid. The difference between the total protein and the globular protein gives collagen. (iii) The filtrate from the removal of the total protein in (ii) contains non-protein nitrogen, which is low, since some of it is occluded in the precipitate.

Collagen has again been the object of many investigations. Gustavson[4] has compared the properties of fish and mammalian collagen. Determinations of shrinkage temperature, acid-combining capacity, and the degree of degradation in urea solutions were made; the combination of both types of collagen with sulpho-acids reacting principally by means of electrovalency on the one hand, and high-molecular compounds reacting through auxiliary co-ordinate forces on the other, was studied. The results obtained led to the conclusion that in mammalian collagen the cohesive forces are mainly hydrogen bonds, with salt links participating, whereas in fish skin collagen salt links predominate, hydrogen bonding playing only a very subsidiary role.

Collagen is one of the two major components of cartilage, the other being chondroitin sulphate.[5] Complex formation between the two exists over a p_H range of 5–9; possibly the chondroitin sulphate plays a part in the organization of collagen in developing connective tissue.

The composition of collagen has received attention. Schneider[6] has detected glucose, galactose, glucosamine, and an unknown compound similar to Bertho's glucosamine peptides, although no indication is given as to the form in which the sugars occur in the protein.

As a preliminary to all experimental work on collagen, especially determination of amino-acid content, it is necessary to obtain as pure a sample as possible. With this end in view Cassel and Kanagy[7] studied methods available for purification, the course of the changes taking place being followed by amide determinations, titration curves and electrophoretic measurements. They reject preliminary treatment with trypsin which, they claim, modifies the collagen in such a way as to cause degradation in subsequent processes. They recommend soaking in 5% salt solution, followed by treatment with half-saturated lime to remove the mucoid. A method is also given for reducing the mineral content to a minimum by washing with distilled water for four days; the collagen obtained can then be used for preparing ash-free gelatin for experimental work.

The basic and dicarboxylic acid contents of collagen have been redetermined by Stubbings and Theis,[8] using chromatographic and colorimetric methods. Their figures for the basic acids determined agree reasonably well with other published data, but the dicarboxylic acid

content is higher than that usually reported from analyses carried out by gravimetric procedures.

	Aspartic acid	Glutamic acid	Arginine	Lysine	Histidine
Theis[8]	6·0	11·6	8·7	5·4	0·8
Gravimetric methods ..	3·5[9]	5·7[9]	7·69[10]	4·12[10]	0·3[10]
		9·75[11]	7·29[10]	3·78[10]	0·36[10]

In this connexion, the results obtained by Graham *et al.*[12] are of interest. Using microbiological methods on bovine Achilles' tendon and gelatin, the figures they obtained were: for the tendon, 6·9% aspartic acid and 10·4% glutamic acid; and for gelatin, 6·7% aspartic and 11·5% glutamic acid. Bowes and Kenten[13] have also redetermined the glutamic and aspartic acid content of ox-hide collagen and found them to be twice the values (5·8% and 8·4%) of Dakin for gelatin.[14] Calculations made from titration curves agree with analytical figures and the minimum molecular weight is calculated as 39,000.

To ascertain whether any difference exists in the amino-acid content of collagen at intervals through the thickness of the skin, Stubbings and Theis[15] split a steer hide into ten horizontal layers and determined the dicarboxylic and basic acid contents of each layer separately. The principal difference occurs in the case of lysine, the surface collagen layers containing 3·76% and 4·20%, while the centre layer contains 5·65%; none of the other acids determined shows any significant variation. The suggestion is made that chemical changes during growth are responsible.

The reaction of collagen with various reagents (other than tanning agents) has been studied by Stubbings and Theis[8] and Bowes and Kenten.[16] The former confirmed previous reports that on treatment with lime there is no change in the total number of amino and carboxyl groups due to hydrolysis of the polypeptide chain, although there is a destruction of amide groups which proceeds more rapidly in the presence of NaOH. Bowes and Kenten also report that the main reaction taking place at p_H 13 is the hydrolysis of amide groups; guanidino groups are modified to some extent to give ornithine and urea, or citrulline and ammonia. It is suggested that a small increase in the number of basic groups is due to breakdown of peptide links, possibly those involving proline and hydroxyproline. Hydroxy-acids are unaffected. Similar changes take place in skins treated commercially. The same authors[17,18] have investigated the effect of deamination and esterification by Me_2SO_4 and MeBr upon the reactivity of collagen, especially towards tanning agents (*see* below). The Sakaguchi reaction is only partially successful in modifying the guanidino groups, 50% of the arginine being destroyed, but deamination with nitrous acid removes all the amino groups and 20% of the arginine. The carboxyl groups are methylated, and some *N*-methylation occurs with MeBr.

Electrophoretic measurements have been made[19] on collagen modified by tanning agents, as well as by deamination and denaturation. The cell used was the horizontal micro-electrophoresis cell of Abramson.[20] The iso-electric point of untreated collagen was found to be 7·0, this being

reduced to 4·6 by deamination (method of Thomas and Foster[21]). The combination of collagen with basic chromium sulphate lowers the iso-electric point, which reaches a minimum when the combined Cr_2O_3 is 1·8%. Three explanations are offered: (i) inactivation of the amino groups through combination with the chromium ions; (ii) some other mode of combination which imparts negative charges to the protein surface; (iii) the chromium complex combines with both the carboxyl and amino groups in equivalent proportions; since the basic groups are stronger,[22] the iso-electric point is lowered. It is postulated that after 1·8% Cr_2O_3 has combined a different type of reaction comes into play. Chrome tanning of the deaminized collagen effects no change in the iso-electric point, i.e. the charge on the complex does not alter the electrophoretic characteristics of the collagen; this opposes (ii) above, and supports (i). In the case of vegetable tannage, the iso-electric point is lowered to 3·2, which could be due to the production of a negatively charged surface by adsorption of the tannin, as well as inactivation of the amino groups, the former predominating. Formaldehyde treatment reduces the iso-electric point, the amino groups being inactivated. Heat-shrunken collagen also has a lower iso-electric point due to surface changes following collapse of the chains.

The shrinkage of collagen is claimed by Weir[23] to be a rate process involving a reaction of the first order. Values of heat, entropy, and free energy are: 141 kg.-cal./mol., 349 cal./mol./deg., and 24·7 kg.-cal./mol. at 60° C.; all decrease in acid or alkali. All tannages, except chrome, reduce entropy more than heat, and free energy increases. An interpretation of these figures is given in the light of the modern theory of protein structure and cross bonding.

The isotherms for water vapour adsorption on collagen, and formaldehyde-, quinone- and chrome-tanned collagen have been measured.[24] Equilibrium is attained more rapidly by adsorption than desorption; dehydration by oven drying effects an irreversible change.

The use of the electron microscope is steadily adding to our knowledge of the structure of the collagen molecule. Wolpers[25] has shown the presence of cross-striated opaque and transparent bands with axis periodicity of 640 A., the opaque band consisting of two dark discs separated by a light band. In some cases each disc can be separated into a doublet so that each period consists of four lamellae separated by three lighter bands, especially in collagen from young people. Two explanations have been given by Zahn[26] for the way in which peptide chains are folded in collagen; (i) one stretched chains and two folded chains (ii) a continuous folding at right angles to the plane of the chain.

An interesting paper by Buechler and Lollar[27] is concerned with keratin. These authors have determined the cystine and methionine content of cattle hair on the one hand and the corresponding epidermis on the other. Separation of the two was accomplished by hand after treatment of the skin in salt solution for several days. Analytical results show that whereas in the hair all the sulphur can be accounted for by cystine and methionine, in the case of the epidermis only 18% of the total sulphur is due to cystine. It is suggested that the missing sulphur may be present in the form of a sulphur-containing organic compound intermediate in the

conversion of methionine to cystine in the process of keratinization. In any case the two proteins are not the same. In this connexion the paper by Stoves quoted in this place last year[28] is of interest. In view of this it might be necessary to reconsider those theories which attribute unhairing to a breakdown of the disulphide link, some of which are reviewed by Bowes.[29]

Vegetable tanning materials and vegetable tanning

Several reports on hitherto little used sources of tanning materials have appeared, especially in the United States. Pine bark waste from pulp mills in the Tennessee Valley has been investigated[30] and found to contain over 5% tannin which gives a satisfactory leather. Hubbard and Kurth report on Douglas fir bark tannin,[34] and give some indication as to its constitution. It is a phlobatannin, and there occurs with it an appreciable amount of dihydroquercitin. The tannin from oak slabs from sawmill waste has received attention,[32] and the conditions of storage and extraction are discussed.

Reviews of native tanning materials have been published in some tannin-producing countries, notably Australia[33] and Germany.[34] In the former, papers of general interest appear on the sulphiting of mimosa bark extract, the improvement of Redunca wood (myrtan) by utilizing a synthetic tannin to assist dispersion, and a method of using mangrove bark to give a leather of satisfactory colour.

White[35] has applied a solubility-curve technique to the study of quebracho. The number of components in a mixture is calculated from the number of changes of slope in the solubility curve of the mixture dissolved in a suitable solvent. By the application of Thorp's graphical method the proportion of each component can be calculated; in this way, quebracho extract is shown to contain five major components. Component *A* corresponds to the insolubles; component *B* is entirely tannin, and probably consists of flavones and flavone glucosides, and not catechins. Components *D* and *E* also contribute to the tanning capacity of the extract. Running paper partition chromatograms of the material dissolved in a butanol/water/acetic acid mixture as solvent indicates the presence of nine fluorescent substances. In addition sugars, gallic acid and an aldehyde have been detected. These results indicate that the nature of quebracho tannin is far more complex than has been thought hitherto.

Burton [36] and Atkin and Burton[37,38] have commenced the publication of a series of papers on vegetable tanning which are likely to prove of great importance in the elucidation of the reaction taking place. The first two papers are concerned with the problem of acids and salts in tanning liquors and their determination. In the first paper a comprehensive review is given of the methods proposed for determining these constituents, and a number of them have been investigated as to their accuracy by carrying out determinations on freshly prepared liquors with and without the addition of known amounts of formic acid. The constitution of the liquors complicates the problem considerably. It is necessary to distinguish, for example, between tannin acidity on the one hand, and natural acidity, i.e. acidity not due to tannins, on the other.

In the case of salts, a distinction must be made between salts of strong and salts of weak acids. Moreover, some of the natural acids may be present in a partly neutralized form, and some of the tannin acids may also be partly neutralized.

Of the methods proposed from time to time, the following have been most used in this country in recent years : (i) the use of a cation-exchange resin in conjunction with titration to a predetermined p_H with alkali (ii) the determination of sulphate in the sulphated ash for estimating the total salts (iii) the determination of the alkalinity of the ash to determine the salts of weak acids. Forward titration with alkali determines a proportion of the acid groups present depending on the end-point chosen; if the titration is taken to too high a p_H, some of the OH groups of the tannin titrate. Back-titration with a strong acid measures the amount of salts of weak acids present; again the end-point is arbitrary, but a p_H of 2 is considered to be adequate for control purposes. The alkalinity of the ash gives, with the liquors considered, results higher than back-titration. The method using a cation-exchange resin[39] gives low results for total salts in liquors containing pyrogallol tans.

In the second paper, these problems are examined more fully. Titration curves were carried out on a range of liquors prepared from a number of tanning materials, and considered in the light of what is known regarding strong and weak acids. (A review of this subject is contained in the paper.) On the basis of the curves obtained, the end-point of the forward titration was taken at p_H 5·8, which avoids titrating OH groups, and obviates errors due to carbon dioxide present. In the determination of weak acid salts by back titration, both p_H 2·0 and 2·8 have been taken as end-points, results using both values being quoted. Figures obtained show that the salts of weak acids (at p_H 2·0) are of the same order as those for total salts quoted by Balfe[40] using the resin method, which is criticized on the grounds that (i) appreciable adsorption of the acids on the resin may take place (cf. Tolliday *et al.*[41]) and (ii) certain acids existing as salts may be precipitated as the insoluble acid on the resin. From data obtained by titration curves it would seem that the salts present in most cases are salts of weak acids. Employing the conception of 'buffer index' due to Jordan Lloyd and Pleass,[42] the results of which are in agreement with Burton and Atkin's, a formula is given for calculating the acids (to p_H 5·8) and salts (to p_H 2·8) from a determination of the buffer index, assuming uniform buffering. Recommendations are made for the application of the titration curve technique to tanyard control using undiluted liquors.

The third paper in the series[38] consists of a discussion of the cohesive forces of collagen, viz. salt link, 'short link,' and resonant forms of the short link. The authors point out that cohesion can be altered by constituents of the tanning liquor such as weak acids and lyotropic salts, and by changes in p_H and temperature; since such changes in cohesion affect the reaction of collagen and tannin, their effect on vegetable tannage can be considerable.

Balfe[43] has also contributed to this subject, and discussed the terms 'strong acid' and 'weak acid' especially in relation to the choice of end-point in titrations. He points out that since the end-point is arbitrary, debate

as to the relative merits of, say, p_H 5·8 or 6·5 as an end-point is not justified. On the question of the effect of dilution involved in the determination of salts by the resin method, he suggests that for tanyard control the error accruing is not important. Replying to Tolliday *et al.*[41] and Atkin and Burton, Balfe claims that errors introduced into the salt determination by adsorption of acids on the resin are not material except in certain cases which are easily recognized. He states that the presence of sparingly soluble acids or their salts in liquors has not been demonstrated. (Atkin and Burton mention chebulinic acid in myrobalans.) A conductimetric method is described involving titration in acetone solution. Florin[44] has provided experimental results which indicate that the dilution factor makes little difference in titrations of acids present, the acid content of various liquors determined before and after dilution being the same within the limits of experimental error.

Holmes and Lee[45] have evaluated the influence of the type of tanning material on the bound water in leather, by measuring the equilibrium between the leather and air at various humidities. Myrobalans leather was the driest at all relative humidities, with two exceptions. By plotting per cent. moisture on dry leather against relative humidity, two effects become apparent in the range 80–90% R.H., corresponding to a change in the mode of binding of water. Removal of tanning material decreases bound water. Up to 80% R.H. the uptake of water by leather is proportional to the square root of the aqueous tension. In a subsequent contribution[46] the same authors have demonstrated a proportionality between the degree of tannage and a fractional power of the external concentration. At 2° c. degree of tannage follows the order myrobalans > chestnut > mimosa > sulphited quebracho; at 20° c. the order is the same except that chestnut slightly exceeds myrobalans; at 38° c. the value for myrobalans drops considerably, the others remaining the same, due to the tendency of myrobalans leather to decompose at the higher temperature; there is also free acid remaining between the fibres. Results obtained with mimosa tannage supported the view that drying fixes tannin. The bearing of these results on tanning is discussed.

The two extreme theories proposed to account for vegetable tannage are, on the one hand, that it is due to salt formation, and on the other, to hydrogen bonding. Gustavson has carried out a great deal of work in support on the first. Experiments[47] on the tanning of collagen unmodified, and with the basic groups inactivated by lignosulphonic acids, show that in the latter case there is a decrease of from 22 to 33% in the tannin fixed; the difference gives the proportion of tannin fixed ionically and otherwise. In the case of sulphited quebracho, for example, on Gustavson's figures, 20·2% tan is fixed to the basic groups, and 45·5% to the non-ionic groups. Di- and tri-nuclear naphthalenesulphonic acids are displaced from collagen by tannins; lignosulphonic acid is not. Evidence from shrinkage temperature measurements indicates that bonding of adjacent amino groups takes place with sulpho-acids. Sulpho-acids containing a large number of OH groups satisfy both electrovalent and co-ordinate valencies, and the affinity of collagen tanned with these compounds for vegetable tannins is lost. In connexion with this work, it has been pointed out[48] that drying collagen in the form of hide powder reduced

the binding capacity for lignosulphonic acids, although the acid-combining capacity is unaltered. This is especially the case in tanned hide powder, where secondary changes take place in the tannin-collagen compound. Bowes and Kenten[18] have also contributed to this problem by tanning deaminized and methylated collagen. They found that deamination decreased the fixation of tannic acid and mimosa by about a half, whereas esterification increases fixation, especially in the p_H range 3·0–6·0, illustrating the relation between tannin fixation and the charge on the protein.

In connexion with the hydrogen bonding theories, Gustavson[49] has discussed the reaction of dihydric phenols with collagen. Doherty and Retzsch[50] claimed that whereas adsorption of the 1 : 3- and 1 : 4-compounds took place, the 1 : 2-compound was inert towards collagen; this was explained by Shuttleworth and Cunningham[51] as being due to chelation of the adjacent OH groups. In support of his own belief that these opinions are incorrect, Gustavson cites the work of Herzog and Adler[52] and Gerngross,[53] who showed that catechol and 1 : 2-dihydroxybenzaldehyde tan, whereas catechol monomethyl ether (guaiacol) and the monomethyl ether of 1:2-dihydroxybenzaldehyde (vanillin) do not. This supports the view that the tanning power resides in the adjacent OH groups. Gustavson's own experimental work lends additional support, since treatment of calfskin strips for 24 hr. in catechol solutions of increasing molarity produces a degree of leathering, and, in 2M. solutions, a fixed catechol content of 6%. No difference was observed in the acid-binding capacity of the treated strips. The bearing of this in the light of the hydrogen bond concept is discussed.

Kutyanin[54] has sought a relationship between the analytical figures for fixed tan, bound water solubles and free water solubles of leathers tanned with various tanning agents, and the constitution of the agent, especially the ratio of OH groups to carbon atoms. Where this ratio is low (lignosulphonic acid, β-naphtholsulphonic acid), the bound water solubles are low, due, it is claimed, to the absence of hydrogen bonds available for co-ordination to the peptide chains. In these cases also the loose water solubles are twice the amount of fixed tan. In the case of quebracho, where the ratio OH/C is high, fixed tan is high compared with easily removed water solubles. There is a decrease in the quantity of bound water solubles after tanning at p_H 8, since hydrogen bonding is prevented by removal of hydrogen ions from the OH groups which commences in this region.

Although the problem regarding vegetable tannage seems no nearer solution, evidence being available in support of the protagonists of both theories, it is reasonable to assume that both hydrogen bonding and salt linking are involved in the process to a varying extent depending on conditions. It should be borne in mind also that the physical changes occurring in the skin attendant upon changes in p_H, as distinct from changes in the charge on the protein, play a part, and in this connexion, the 'accessibility' theory of Braybrooks, McCandlish and Atkin[55] is of interest. The point has also been referred to above, in discussing the work of Atkin and Burton.[38]

Merrill *et al.* have extended their work on the reaction of tannins with

collagen in solvent–water systems. In earlier contributions[56,57] they showed that in stripping vegetable tanned leather with various solvent/water mixtures, no end-point is reached, the tannin remaining in the leather at any given time varying with the solvent and other factors. It was assumed that tannin contained in a solvent/water system would combine with collagen to an extent in inverse proportion to the stripping power of the same system. This assumption has been verified experimentally.[58] The conclusion is reached that stripping in aqueous solvents results from the displacement of the equilibrium between tannin combined with collagen and tannin in solution. On the other hand, although anhydrous solvents do not remove any tannin, uptake from such a system is negligible : the presence of water is necessary for both tanning and stripping.

The tanning potentialities of magnesium lignosulphonates have been assessed by Kremen and Lollar.[59,60] Leather was obtained comparable in physical and chemical characteristics to that produced by natural tannins. Comparisons were also made between leathers tanned with purified and commercial quebracho and mimosa; little difference was found in the quality of the leather produced.

The use of formic acid in the acidification of mimosa tannages is dealt with by Cheshire,[61] in order to ascertain how far it might be used to replace lactic acid. He reports however that the leather is deficient in firmness, if the acid is used in safe quantities. Damage due to using too much is especially noticeable in cases where hot-pitting is a part of the manufacturing process, taking the form of loss of tensile strength and hide substance. The limiting concentration of total acidity appears to be about 0·2 N.

Chrome tanning agents and chrome tanning

Shuttleworth has continued his studies on chromium cations.[62] Previous work had shown that boiled and aged chrome-alum solutions were mixtures of electrovalent non-basic sulphate and one-third basic chromium sulphate, and that the latter titrates to the two-third stage before the titration of the non-complex bound ionized sulphate. Using his well established conductimetric titration technique, he has shown that the titration from the one-third basic complex to the two-third stage takes place over a range where only a small proportion of the electrovalent sulphate titrates. Evidence from crystal separation suggests that the former has a definite entity. In high dilutions part of the complex sulphate becomes ionic, being replaced by olated OH groups. Olation is greater at higher concentrations : this increase in particle size is responsible for precipitation at lower basicities in these cases. In mixed complexes, since sulphate groups in the complex are more readily replaced by OH ions than are bound water molecules, the bound sulphate titrates before the electrovalent sulphate with alkali. At higher temperatures, the increased rate of collision causes complex formation to take place more rapidly. At the same time, the water molecules become less firmly bound. Structural formulæ are given for the non-basic and basic sulphates.

The penetration of organic ions into the chrome complex is the basis of a well-known practice in leather manufacture. In work carried out on this subject by Serfass and Theis[63] and many others, marked differences in the behaviour of the hydroxy-organic acids have been observed. Shuttleworth,[64] commenting on this, shows that acidic complexes are formed by the action of the salts of hydroxy-acids on chrome alum, owing to ionization of the co-ordinated OH group. The five-membered ring is very stable. (The formation of such a ring explains the stripping action of salts of hydroxy-organic acids on chrome leather.) Plant[65] and Shuttleworth[66,67] have engaged in a controversy on this question of the penetration of the complex by anions, especially with regard to the relationship of the dissociation constant of the acid and the stability of the complex produced.

Theis *et al.*[68] have extended their spectrophotometric studies of complex chromium salts to those containing added hydroxyacetic, monochloracetic, aminoacetic and acetic acids, the effect of the time and concentration being noted. The extinction values assumed by the various solutions at 420 and 580 mμ. are considered to represent the degree of protection afforded by the penetrating anion. On this basis the relative order of penetration is glycine > glycollic acid > acetic acid > monochloracetic acid. It was noted that glycine shows greater penetrating power than the hydroxy-acids tartaric and citric. The results confirm earlier work[69] from ion-exchange data.

The influence of resorcinol, hydroquinone, pyrogallol and gallic acid on chrome complexes has been the subject of a paper by Kubelka.[70] Resorcinol and hydroquinone do not cause any change in the complex bound sulphate. Pyrocatechin, by expelling sulphate groups, increases the positive charges on the complex. Both pyrogallol and gallic acid enter the complex at the expense of sulphate groups, while tannins, especially at the boiling point, enter the complex readily; e.g. 5% tannin forms an anionic complex.

Pressley[71] has related chromium content to the water-penetration pressure and shrinkage temperature using a range of concentrations of chromium chloride at various p_H values on sheepskin. The relation of the p_H of, and chromium concentration in, the tanning bath to the chromium content of the leather produced is shown by a series of contour lines, from which can be read the p_H and liquor concentration necessary to give the leather any particular content of chrome oxide. These show that in the case of chromium chloride uptake of chrome is more sensitive to changes in p_H than in the case of chrome sulphates. Conditions of tanning have no effect, as such, on penetration pressure or *Ts*; chloride tanned leathers, however, in all cases, showed higher penetration pressures than sulphate leathers. Maximum *Ts* (93° c.) was obtained with 2·5% chrome oxide content on skin. Extending this work to chromium sulphate liquors with added sodium sulphate and chloride,[72] it was shown that penetration pressure increased with chrome content of the leather using a mixed liquor, i.e. one containing both sodium chloride and sulphate, the pressures obtained being lower at all points than in the case of leather tanned with chloride liquor alone. Penetration pressure increases, and *Ts* decreases with ageing.

Mineral tannages other than chrome

Aluminium.—Alum retannage of insole leather has been carried out by Beebe *et al.*,[73] who find that resistance to moist heat and moulds is increased, while water absorption and elongation are decreased. Difficulties encountered, viz. obtaining an Al_2O_3 content of more than 3·0%, and an even distribution throughout the thickness of the leather, were overcome by the use of masking agents. Laboratory experiments, in which the masking agent was added to the tanning liquor immediately before use, showed that sodium citrate was the most efficient of these. In the case of liquors made up and used under practical conditions, where the salt was added some time before use, gel formation set in and rendered the citrate masked liquors useless. Sodium acetate in the ratio of one mol. acetate per mol. Al_2O_3, however, proved satisfactory, and tanning in a bath containing 10% Al_2O_3 on skin weight over an increasing p_H range of 3·8 to 4·8 gave a leather with a content of Al_2O_3 of 4% and a shrinkage temperature of 115–117° c.

Alum tannage has been discussed by Pal and Das[74]; they found increasing aluminium uptake with increasing concentration in the tanning bath, while they claim that the use of sodium sulphate increases this uptake further and increases the shrinkage temperature. The last factor is more dependent on the basicity of the salt adsorbed than on the quantity.

Iron.—Sporadic attempts have been made over a number of years to utilize iron salts as tanning agents, and research into the problem was stimulated afresh by the war, during which several papers appeared, especially in the United States. An argument which has often been urged against the manufacture of iron-tanned leather is that it is subject to comparatively rapid deterioration due to oxidation, although Kanagy[75] found no evidence of this in experiments carried out with the oxygen bomb; this was later confirmed by Tu.[76] In later years, several reports have been published in France. In the most recent contribution to the problem, Thorstensen and Theis[77] point out that the difficulty all along has been to overcome hydrolysis and precipitation of basic salts and hydrated oxides. They have carried out new experiments, and determined by titration curves the likeliest masking agent for solutions of ferric sulphate, as a preliminary to practical tanning tests. These were carried out on rabbit skins, the optimum conditions, determined in preliminary trials, being a Fe_2O_3 concentration of 5% on skin weight, and a p_H range of 3·25–4·25, with the masking agents employed. The most efficient masking agents were the salts of the hydroxy-organic acids; the more hydroxy groups present in the molecule, the better the leather produced. Conditions were designed to give as even a distribution as possible of iron throughout the skin.

Successful iron tannages using non-basic ferric sulphate and sodium silicate have been reported from France,[78] and have been used on both heavy and light leather. The statement has also been made that the wearing properties of such a leather are superior to those of vegetable tanned leather.[79]

Zirconium.—The only contribution to appear during the year comes from Somerville and Rau.[80] Tanning tests were carried out with sodium

zirconium sulphates on pickled skins with satisfactory results. Evidence is presented that in tanning the zirconium is present in a cationic form.

Miscellaneous tanning agents and synthetic tannins

The danger that natural tanning materials may become insufficient to meet tanners needs at some future date by reason of economic, political or natural forces, is leading leather chemists to explore further the tanning possibilities of synthetic compounds as substitutes. For example, Patterson and Jurney have presented papers[81] on aliphatic sulphonyl chlorides: this follows work in Germany during the war.[82] The most convenient way of preparing these compounds is by the Reed process[83] in which sulphur dioxide and chlorine are reacted with the hydrocarbon in the presence of actinic light. Combination of the sulphonyl chloride with pelt occurs during drying at 40° c., after the material has been drummed into the leather in the presence of an acid acceptor, e.g. sodium carbonate. The maximum sulphur content of the tanned collagen (hide powder in Patterson's experiments) is about 1·2%, corresponding to saturation of amino N according to the figures of Kanagy and Harris.[84] The nature of the bond formed in the process was demonstrated by infra-red spectrometry. The compound was hydrolysed by the method of Gurin and Clarke,[85] which specifically breaks the peptide links, and absorption curves obtained on the purified hydrolysate. Two bands were obtained at frequencies of 1155 cm.$^{-1}$ and 1361 cm.$^{-1}$, which are characteristic of the $-SO_2-$ group. Jurney carried out the practical tanning tests, obtaining satisfactory leathers from a wide variety of skins by drumming with the chloride at p_H 5·5–8·0 in the presence of formaldehyde. The white leather thus produced dyes well, and can be cleaned with solvents or washed with no sacrifice of properties, making it very suitable for gloving and clothing. Its use as a pre-tanning agent is also suggested; since it produces long fibres and an open structure, the leather should be receptive to filling materials.

Synthetic tannins of the traditional type are used for dispersing insolubles in natural tanning material liquors, in combined vegetable tannin–synthetic tannin mixtures, and as tanning agents on their own. For example, work carried out in Germany during the war[86] described methods for replacing oak bark extract by various synthetic tannins; the tanning and binding values of the mixtures were higher than either of the components used singly, and increased with increase of syntan in the mixture; in general insolubles were decreased. Anderson[33] used syntans to improve the properties of myrtan (Redunca wood extract), a material which used alone deposits large quantities of sludge in vats. Additions of syntan up to 10% caused a decrease in insolubles from 4% to 1·5% at p_H 3·0; in practice, blends employing 6% of the syntan can be employed with no sacrifice of leather quality. Similarly, shortage of natural tannins in Germany led to experiments on replacement of these by synthetic products in the manufacture of all classes of leather, in amounts up to 50%, the properties of the leather being in no case poorer, and in some cases better than, that made from tannins alone.[87]

Sole leather has been tanned by Marshall and Turley[88] with syntan only, using a method analogous to that employed using normal tanning

agents. The leather obtained is stated to compare favourably in physical and chemical characteristics to vegetable tanned sole.

Analytical methods

New and modified methods of analysis which could be applied to materials used by the leather industry are too numerous to mention in full. However, papers of direct interest have appeared. In the tannin analysis field, Hough[89] has proposed as a qualitative reagent for tannins a 2% aqueous solution of polyvinyl alcohol which, with or without the addition of acetic acid or sodium sulphate, distinguishes between certain tannins, or natural tannins and syntans, by means of precipitation. A method for identifying tannins which depends on their reducing properties and heavy metal salt formation has been developed.[90] The standard methods for the quantitative analysis of tannins have received attention and criticism, and new ones have been proposed. Jany[91] has compared the shake method and the filter-bell method on different materials at different dilutions; his conclusions justify the continued use of the former. The chief disadvantage of the procedures which have been adopted as official methods by the various societies lies in the time taken to carry them out, and it is not surprising that attempts should be made to develop more rapid methods. Lattey[92] makes use of the gelatin–tannin reaction for a quick though approximate estimation of tannin present in solution, while a modification of the Löwenthal permanganate titration has been suggested with the same end in view.[93] A spectrophotometric method is described by Adams and Merrill,[94] using the Vorsatz technique. The optical density at 400 mμ. of a tannin solution treated with sodium nitrite, acetic acid and sodium hydroxide is a linear function of the tannin content although the relation is different for every material, so that in analysing blends the standard must contain the same materials in the same proportions as the mixture under examination. The colours produced by individuals in a blend are additive. It is claimed that the precision of the method is about 1·5% in the O.D. range 0·300–0·500. Many analytical problems are being approached in a fresh light, making use of modern apparatus. For example, the application of polarography to such problems is reviewed by Lollar and O'Flaherty,[95] who apply it especially to chromium compounds, while the same method has been examined in relation to vegetable tannins by Browning.[96] Quebracho, mimosa, mangrove, chestnut and myrobalans are reducible at the dropping mercury electrode giving a wave with a half-wave potential of $-$ 1·0 v., and with the exception of mimosa, a second wave reduction at $-$ 1·3 to $-$ 1·6 v. Phenols and acids related to the structural units of the tannins give reduction waves in the neighbourhood of $-$ 1·0 v. after ageing. Mathews and Borders[97] have described a high-frequency oscillator and the potentialities of its use in research and control have been examined, e.g. in the rapid determination of tannin, rates of enzyme action, acid-binding studies on proteins, nitrogen determinations, etc.

A method for the estimation of insolubles in tannin solutions which, it is claimed, is more accurate than that usually employed, has been described by Haglund.[98] It involves removing the suspended matter

by centrifuging, and weighing the material thrown down before and after drying, the result being obtained by making use of an equation.

In the analysis of sulphite cellulose waste liquors and lignosulphonates, Salvesen and Hogan[99] recommend neutralization of the solutions before evaporation to dryness to prevent the loss of volatile acids. A method is also given for the determination of sulphur and cations.

On the continent, work has been carried out on the analysis of synthetic tannins. A modification of the Stather-Herfeld method (a shake method using hide powder) has been suggested[100]; the tanning value is defined as the amount of material taken up by 100 g. of the powder after shaking. In a subsequent paper, the use of small-scale tanning tests is advocated, followed by a comparison of the physical properties of the leather with those of vegetable leather tanned under the same conditions.[101] Two methods for the investigation of syntans have been investigated by Kubelka[102] *et al.*, viz. the Stiasny method of fractional salting-out, and the Stather method, in which the tannin removed by an addition of salt is determined by the Löwenthal method. The latter method is recommended, and of several precipitants tried sodium chloride proved the most suitable. In using the Stiasny method, 11, 22, and 33% of salt was added to 100 ml. 1% syntan solution, and the tannin content of the precipitate at each stage determined. The higher the sensitivity to salt, the fuller is the tannage obtained from the material. Two difficulties associated with the filter-bell method for syntan analysis are discussed by Kuntzel and Bosse.[103] They show that the difficulty of obtaining constant weight on evaporating solutions may be overcome by neutralizing them first. Non-tannin residue after detannization often shows a positive gelatin test indicating, it is usually assumed, the presence of tannin. The gelatin-precipitating compounds present are not, however, necessarily tannins and the claim is made that the detannized solutions contain a 'semi-tannin' capable of precipitating gelatin but incapable of tanning skin. Curves of purity (i.e. tannin/total solids) against total solids for chestnut and syntans have been compared; in the first case the relationship is constant up to a point at which tannin begins to appear in the detannized solution under the conditions of the analysis, corresponding to a 2% solution, whereas in the case of syntans constancy is maintained only up to a solids concentration of 0·18%. Criticisms of this are answered in a subsequent paper.[104]

Turning to the subject of leather analysis, simple and well established methods have come in for discussion which would suggest to the uninitiated that they are not as straightforward as they appear. One of these is the determination of nitrogen in leather and proteins, especially as regards the catalyst used in the digestion. Hiller *et al.*[105] obtain the same figures for the nitrogen content of proteins as those obtained by the Dumas combustion method, but by employing mercury as a catalyst. Kubelka and Ferbas[106] in a preliminary paper recommend the use of a mixture of selenium, copper sulphate and mercuric oxide, with which digestion is complete in twenty minutes. Attention is drawn to sources of error arising in the digestion. Hindin and Grosse[107] propose the use of the mass spectrometer for the analysis of the gaseous products

of the Dumas combustion, an inert gas being used as internal standard; the method is still in the experimental stages.

Moisture.—The application of the Karl Fischer method to the determination of moisture in proteins has been made by McComb[108] using hair, soya bean protein, zein, and casein. Results are not in all cases comparable to oven methods, e.g. in the case of casein; in any case, severe difficulties are likely to be met with on applying the method to leather. A rapid means of measuring moisture content of leather is described by Kremen,[109] by a correlation of moisture content with high-frequency dielectric constant; an apparatus is used which gives accurate results over a wide moisture range.

A Committee set up by the A.L.C.A. has presented a report on analytical methods for veg–chrome leather.[110] In determining the chrome in this type of leather the wet oxidation method is to be preferred[111]; the factors which have to be taken into account in interpreting analytical results are discussed.

A wide variety of methods for the determination of metallic cations might find application, e.g. a colorimetric method for iron making use of the blue colour produced with *iso*nitrosodimethyldihydroresorcinol estimates the element in the presence of many other cations and anions,[112] and the determination of aluminium in the presence of chromium by aluminon.[113] Wolstenholme[114] makes use of the coloured compound formed by iron and thioglycollic acid in the presence of ammonia for determining iron in chrome liquors. The chromium is prevented from interference by locking into a complex with citric acid. A method for the determination of zirconium is of interest in view of the developments in this tannage. The metal is precipitated from HCl solution by trimethyl phosphate, followed by heating for twelve hours, and ignition at 900° C. to produce zirconium pyrophosphate, which is weighed. Copper, especially in tanning extracts, can be estimated polarographically[116]; another method[117] measures the colour produced by potassium ethyl xanthate in a neutral solution of the ash after removal of iron and aluminium.

The application of synthetic resins to leather

Increasing interest has been shown during the last decade in the potentialities of synthetic resins for both tanning and impregnation; in the latter case attention is particularly focused on the possible improvements of physical properties such as wear resistance and water penetrability. The subject is well reviewed by Cheronis *et al.*[118] in so far as it applies to the factor of water repellency. They point out that whereas in the case of textiles improvement can be made by chemical modification of the fibres, this is impossible in the case of leather yet, so the desired end is attained by depositing a hydrophobic polymer over and between the fibres. Broadly speaking two methods are available: introduction of the material in the form of an emulsion, or in solution in an organic solvent. In either case, polymerization may precede or follow impregnation. Of these methods, the emulsion technique is preferable. Preliminary experiments have been carried out with a view to assessing

the increase in water repellency imparted to gloving leathers by a number of resins. The tests were applied to horse hide, and water repellency assayed by static and dynamic methods; a new test was designed to reproduce conditions likely to be met with in practice. Attention has been paid to the organo-silicon polymers, with the following results: (i) the organo-silicon oils improve static water-repellency, but the result is not maintained on flexing, even with the incorporation of up to 40% polymer; (ii) the best results were obtained with polymers made by hydrolysing a mixture of di- and tri-functional chlorosilanes, dissolving the product in a solvent, and emulsifying; (iii) 5–10% deposition is adequate for the purpose. A method is also discussed for the preparation of polyaminosilane by the ammonolysis of chlorosilanes. It is pointed out that the high cost of these products would militate against their acceptance, and a report is promised on the use of resin polymers of the polyester type.

Hough[119] has employed water soluble urea–formaldehyde condensates to precipitate the water solubles in sole leather, with a resultant gain in firmness and wear resistance, and decreased water uptake. The main objection of using such a condensate, which is alkaline, has been overcome by making use of the reaction between boric acid and polyhydroxy compounds; on application of a boric acid/condensate solution to the leather, a reaction takes place between the acid and the tannins in the leather with a consequent drop in p_H *in situ*. Experimental evidence indicates that for any given tannage there might be a critical ratio of boric acid to condensate. A further point which is noted is the effect on analytical figures obtained from the treated leather.

Experiments on the polymerization of a monomer *in situ* are described by Oehler and Kilduff.[120] They used as catalyst benzoyl peroxide, and polymerized in a closed chamber at 70° C. A maximum increase in abrasion resistance is obtained by polymerizing *n*-butyl methacrylate *in situ*, and applying solutions of *n*-butyl methacrylate and ethyl acrylate copolymers effects no change. On the other hand both *in situ* polymerization and solution-impregnation decrease water absorption in the case of both vegetable and chrome upper leather.

There is no line of demarcation between synthetic resins and synthetic tannins, since the latter are merely a special class of soluble synthetic resins, and have been known for over thirty years. The term 'synthetic' does, however, connote a definite type of product, of which phenol–formaldehyde condensates are the best known example. Attempts to use such products as tanning agents have been made from time to time, e.g. Highberger *et al.*[121] have used resorcinol–furfuraldehyde condensates. Hough,[122] in a paper on the tanning properties of water-soluble phenol–formaldehyde condensates, describes the preparation of such a compound by condensing 1 mol. of phenol with 1·5 mols. of formaldehyde, in the presence of 48 millimols. NaOH at 70° C. for 150 minutes. The introduction of boric acid into the tanning bath produces a leather softer and fuller, and the optimum p_H of tanning is about 8·0 at the commencement and 5·0 at the end of the process. The degree of tannage obtained (resin uptake per 100 parts hide substance) is of the order of 68 under optimum conditions, with a shrinkage temperature of 79·5° C.

Formation of the polymer *in situ* may be effected, and Noerr and Hees[123] mention two types of compound: (i) methylol compounds and (ii) certain aliphatic di-*iso*cyanates. In the first case, the hide or skin is treated with 10% of the monomer in solution, and the p_H subsequently reduced to 2·5 until tannage is complete, as determined by the shrinkage temperature. Finally the p_H is raised again to 4·5 in a neutralizing bath. Di-*iso*cyanates are drummed into the pelt in the form of an emulsion, using 2–5% of the material on skin weight; the leather produced has a high tensile strength and is similar to oil tanned leather in appearance and feel.

Physical testing and physical properties

Physical testing has many advantages over chemical methods, since leather quality is often judged by physical characteristics and the tests themselves can, in some cases, be carried out more rapidly than chemical analyses. During the year, a report has been published[124] by a sub-committee of the Society of Leather Trades Chemists, in which methods have been proposed for the determination of thickness, tensile strength, grain strength and extensibility, apparent density and water absorption.

The possible effect of drying methods on water resistance of chrome-tanned upper leather is the subject of an investigation by American workers.[125] Three methods of drying were used: paste drying, i.e. the moist leather being pasted on glass or similar surface, drying on frames under stretch, and drying without stretch. No one method showed advantages over the others either in static or dynamic testing for water repellency.

The influence of moisture content of shoe-upper leather on its elastic properties, and hence the extent to which shape will be maintained in wear, has been determined by Faibishenko.[126] Chrome calf leathers were kept at 30% extension for seven hours in atmospheres of different humidities, the tension being measured at half-hour intervals. The relaxation curves were similar for all moisture levels. Changes in length and tension were measured during drying from moisture contents of 20, 40, 60, and 100%; the higher the moisture content to begin with, the less is the residual tension.

An attempt has been made by Mitton[127] to correlate data from microscopic examination of fibre structure of cross sections of leather with abrasion resistance. Features revealed under the microscope which have a bearing on abrasion resistance are (i) boldness of weave (ii) orderliness of pattern (iii) angle of weave (iv) compactness of pattern (v) fullness (vi) straightness and (vii) non-separation. A statistical examination of data obtained from 131 samples showed that although physical and microscopical data are related, the relationship is not complete enough to allow of assessing abrasion-resistance by microscopical examination alone. The angle of weave and the orderliness of fibre structure seem to be the most important factors involved.

Mitton[128] has also turned his attention to 'run' in gloving leathers. This has always been judged by handle and feel, and quite reproducible results have been obtained in this way. A more exact method is desirable, but the use of the flexometer, although it can yield information when

leathers differ widely in properties, does not distinguish between small differences. Tests were carried out by flexing at axes inclined at various angles to the backbone of skins, and no correlation was obtained.

Compressibility of sole leather.—Kubelka[129] determines compressibility on (i) original dry sample (ii) wet sample (iii) on a sample soaked in water and then dried. Results indicate fullness and also the extent to which the leather will become soft and spongy after soaking. Results using a modified Chambard apparatus (3·5 mm. steel cylinder and 70 kg. pressure) were: dry pit tanned butts, below 16%; drum tanned butts, 18%; pit tanned shoulders 20%: bellies 23%. If differences in compressibility between wet and dry leather are over 30, the leather becomes spongy on soaking. Differences between soaked and dried leather and the dry leather express fullness of the leather after finishing effects have been eliminated by the soaking. Leathers with a value over 15 for this difference will, after wetting and drying, be spongy.

What might be regarded as fundamental work on physical properties has been carried out in the United States. Using kangaroo tail tendon, Compton[130] determined the influence of various tannages on its tensile strength. An increase in chrome content does not seem to cause an increase in tensile strength although it produces a stronger fibre than does formaldehyde tannage, since in the latter case a decrease was obtained proportional to the strength of aldehyde in the tanning solution. Formate-masking of chrome-tanning solutions, however, tends to lead to stronger bundles. A relationship appears to exist between fibre strength and shrinkage temperature, since increase in the latter is paralled by a decrease in the former. This problem was examined by Highberger[131] who pointed out that a mechanical stability factor as well as a thermal factor had to be taken into account; further, the effects of tannage on the mechanical factor are at variance with what one would expect on the basis of the cross-linking hypothesis. Remarks of Gustavson[132] are of interest in this connexion. Pointing out that results on single fibre bundles are likely to be more rational, the complications due to interweaving fibre structure having been eliminated, he stresses the fact that tensile strength determinations on wet fibres should be compared with T_s figures. He quotes figures for fibres tanned with formaldehyde and quinone, in which cases measurements on the dry fibres show a decrease in tensile strength. while on wet fibres an increase of approximately 50% is registered. Both thermal stability and tensile strength are increased under the latter conditions.

Weir[133] measured the coefficient of cubical expansion of collagen and leather by a dilatometer technique. For collagen and all leathers except chrome-vegetable tanned, the figure obtained was $540 \times 10^{-6}/^\circ$ C. Increase in real volume of the leather is linear up to the T_s; during apparent shrinkage an increase in 1% real volume occurs, and is a law of the first order reaction. Concluding from these results that, if leather were suspended in a water-bath, the increased volume would cause an increased buoyancy and therefore loss of weight in a sample suspended from the arms of a balance, Shaw and Maeser[134] carried out work on these lines, and arrived at conclusions somewhat different from those of Weir. Increase in buoyancy was not linear with increase in temperature below

the shrinkage temperature, and decreased sharply when the shrinkage temperature was reached, in the case of leathers not completely dehydrated first. Leathers completely dehydrated before the experiment increase in buoyancy at a lower rate, and show no decrease at the temperature of shrinkage. The loss in buoyancy at T_s in the case of the leathers not dehydrated might correspond to a loss of bound water which, it has been claimed,[135] occurs during shrinking. Observed differences between these results and those of Weir are attributed to differences in the method used in each case.

Miscellaneous

Mycological and entomological problems relating to the leather industry are reviewed by Musgrave,[136] and bacterial problems by Robertson and Haines.[137] Bacterial phenomena asociated with hide preservation, and methods for control, are the subject of a paper by Anderson.[138] Eighty strains cultured from washings from hides and skins were classified into seven groups: *Achromobacter*, 18; *Micrococcus*, 24; *Sarcinae*, 4; *Staphylococcus*, 4; *Bacillacae*, 8; *Rhodococcus*, 2; unclassified, 7. The difference between the various groups in their tolerance towards salt was wide, the *Achromobacter* being sensitive, bacilli fairly tolerant, and all others tolerant. Certain strains develop salt tolerance fairly rapidly, especially *Sarcinæ*, *Micrococci* and *Staphylococci*. A lipase-secreting organism hydrolyses fat, and may lead to stains later. The use of sodium fluoride as a bacteriostatic agent was shown to be sound, growth on agar plates with varying amounts of the fluoride being inhibited completely by concentrations of from 0·1–0·2%. A previous claim often made, that the presence of calcium salts increased growth, was not substantiated in practice.

Little work has been reported on bating. Moore,[139] in a preliminary study, describes new techniques and apparatus for measuring physical changes in the skin, such as fall, smoothness of grain (expressed as 'grain-slip index'), porosity and relative elasticity. It is intended to use these in research into the correlation of laboratory results with the experience of the practical tanner. The evaluation of bating activity of artificial products has been the subject of a contribution by Gustavson.[140] Pretreatment of skin by trypsin renders it partly soluble in hot water. 2 g. calf pelt are treated with 50 ml. of 4% bate infusion, and after washing are immersed in water at 70° C., the solubilized N being determined by Kjeldahl's method. The optimum conditions are discussed. A viscometer method, using gelatin as the substrate, is described by Vlcek and Mansfeld.[141]

The Committee of the Society of Dyers and Colourists on Fastness of Dyes on leather has issued its report.[142] Standard methods for tanning and dyeing are proposed, and the methods of dye examination are, light fastness, penetration, and solubility.

Microscopical examination shows that fatty spue develops in hair follicles and gland openings, and then spreads outwards over the grain.[143] No relationship was found between spue formation and free fatty acid in the fat in the cases of oleic acid and tallow; with cod oil, increased free fatty acid content gave increased spue formation. The presence of glycerol seems to increase spue formation. Work on gummy spue

confirms Balfe's conclusions that it develops between the leather fibres, and is forced out through the hair follicles and grain.

Glue and gelatin

Ames[144] has given a comprehensive account of the manufacture of hide glue and gelatin. Gelatin from the skin of the blue whale was prepared[145] after degreasing with acetone and removal of the crude proteins with salt, soda and water, by extracting with water at progressively higher temperatures. In a patent process[146] the fat is extracted from collagen- or ossein-containing materials by alkali treatment (1–5 parts caustic alkali per thousand parts water), designed to effect emulsification of the fats. The resulting product is bleached before extraction. Freezing of the defatted material is proposed by Chadray[147]; the frozen blocks are then disintegrated, the temperature raised and the resultant paste warmed below 140° F. under 5 to 15 lb. pressure for 2 hours. Fat left in the waste after the alkali treatment is skimmed off, the paste filtered and dried in pans. In place of lime, an American patent[148] uses 1–30% solution of an aliphatic amine for dissolving the collagen.

Ferry and Eldridge[149] show that specific rotation of gelatin gels is independent of concentration, decreasing with increasing temperature and decreasing molecular weight. Rigidity is proportional to the square of the concentration and decreases with decreasing temperature: its square root is a linear function of the molecular weight. It is postulated that the change in optical activity accompanying gelation is due to intermolecular cross links or to an intramolecular rearrangement; a small number of intermolecular links is responsible for rigidity.

References

[1] Dempsey, M. and Garrod, M. E., *Ann. appl. Biol.*, 1947, **34**, 435
[2] Turner, J. N., ibid., 442
[3] Jacobs, J. L., *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 722
[4] Gustavson, K. H., *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 332
[5] Partridge, S. M., *Biochem. J.*, 1948, **43**, 387
[6] Schneider, E., *Kolloidzschr*, 1948, **111**, 96
[7] Cassell, J. M. and Kanagy, J. R., *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 424
[8] Stubbings, R. L. and Theis, E. R., ibid., 178
[9] Schneider, F., *Collegium*, 1940, **839**, 97
[10] Highberger, J. H., *J. Amer. Leath. Chem. Ass.*, 1938, **33**, 9
[11] Rees, M. W., *Biochem. J.*, 1946, **40**, 632
[12] Graham, C. E. *et al.*, *J. biol. Chem.*, 1949, **177**, 529
[13] Bowes, J. H. and Kenten, R. H., *Biochem. J.*, 1948, **43**, 358
[14] Dakin, H. D., *J. biol. Chem.*, 1920, **44**, 499
[15] Stubbings, R. L. and Theis, E. R., *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 157
[16] Bowes, J. H. and Kenten, R. H., *Biochem. J.*, 1948, **43**, 365
[17] Idem, ibid., 1949, **44**, 142
[18] Idem, *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 367
[19] Cassell, J. M. and Kanagy, J. R., *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 442
[20] Abramson, H. A., 'Electrokinetic Phenomena,' Chemical Catalogue Co. Inc. (New York, 1934)
[21] Thomas, A. W. and Foster, S. B., *J. Amer. chem. Soc.*, 1926, **48**, 489
[22] Braybrooks, W. E., *J. Soc. Leath. Tr. Chem.*, 1939, **23**, 73
[23] Weir, C. E., *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 108
[24] Green, R. W., *Trans. Proc. roy. Soc. N.Z.*, 1948, **77**, 24
[25] Wolpers, C., *Makromol. Chem.*, 1948, **2**, 37, via *Chem. Abstr.*
[26] Zahn, H., *Kolloidzschr.*, 1948, **111**, 96

[27] Buechler, P. T. and Lollar, R. M., *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 359
[28] ANNUAL REPORTS, 1948, **33**, 423
[29] Bowes, J. H., *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 176
[30] Snow, E. A., *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 504
[31] Hubbard, J. K. and Kurth, E. F., ibid., 604
[32] Snow, E. A. and Bailey, L. F., ibid., 737
[33] Symposium on the Native Tanning Materials of Australia, 1946
[34] Grassman, W., *Colloquiunsber. Tech. Hochschule Darmstadt*, 1947, **1**, 59
[35] White, T., *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 39
[36] Burton, D., ibid., 1948, **32**, 362
[37] Atkin, W. R. and Burton, D., ibid., 1949, **33**, 52
[38] Idem, ibid., 271
[39] Cheshire, A., Brown, W. B. and Holmes, N. L., ibid., 1941, **25**, 254
[40] Balfe, M. P., ibid., 1948, **32**, 39; also 'Progress in Leather Science,' 1948, **3**, 610
[41] Tolliday, J. D. *et al.*, *J. Soc. Leath. Tr. Chem.*, 1948, **32**, 291
[42] Lloyd, D. Jordan and Pleass, W. B., ibid., 1933, **17**, 352
[43] Balfe, M. P., ibid., 1949, **33**, 197
[44] Florin, O., ibid., 422
[45] Holmes, N. L. and Lee, H., ibid, 21
[46] Idem, ibid., 122
[47] Gustavon, K. H. and Larsson, A., *Papperstidning*, **11B**, 1947; *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 99
[48] Gustavon, K. H., *J. Soc. Leath. Tr. Chem.*, 1948, **32**, 287
[49] Idem, ibid., 1949, **33**, 256
[50] Doherty and Retzsch, *J. Amer. Leath. Chem. Ass.*, 1941, **36**, 442
[51] Shuttleworth, S. G. and Cunningham, G. E., *J. Soc. Leath. Tr. Chem.*, 1948, **32**, 183
[52] Herzog and Adler, *Collegium*, 1908, 178, 182
[53] Gerngross, *Biochem. Z.*, 1920, **108**, 82; *Collegium*, 1920, 565
[54] Kutyanin, G. I., *Legkaya Prom.*, 1948, **4**, 22; *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 345
[55] Braybrooks, W. R., McCandlish, D. and Atkin, W. R., *J. Soc. Leath. Tr. Chem.*, 1939, **23**, 111, 135
[56] Merrill, H. B. *et al.*, *J. Amer. Leath. Chem. Ass.*, 1947, **42**, 536
[57] Idem, ibid., 1948, **43**, 481
[58] Idem, ibid., 1949, **44**, 54
[59] Kremen, S. S., Lipsitz, P., Lollar, R. M., ibid., 1948, **43**, 542
[60] Kremen, S. S. *et al.*, ibid., 1949, **44**, 194, 371
[61] Cheshire, A., *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 314
[62] Shuttleworth, S. G., ibid., 92
[63] Serfass, E. J., Theis, E. R. *et al.*, *J. Amer. Leath. Chem. Ass.*, 1948, **43**, 132
[64] Shuttleworth, S. G., ibid., 1949, **44**, 511
[65] Plant, D. A., *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 146
[66] Shuttleworth, S. G., ibid., 112
[67] Idem, ibid., 328
[68] Serfass, E. J., Wilson, C. D. and Theis, E. R., *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 647
[69] Serfass, E. J. *et al.*, ibid., 1948, **43**, 132
[70] Kubelka, V., *Tech. Hlidka Koz.*, 1949, **24**, 97
[71] Pressley, T. A., *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 4
[72] Idem, ibid., 351
[73] Beebe, C. W. *et al.*, *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 204
[74] Pal, B. C. and Das, B. M., *Tanner (India)*, 1949, **4**, 22
[75] Kanagy, J. R., *J. Amer. Leath. Chem. Ass.*, 1938, **33**, 565
[76] Tu, S. T., ibid., 1948, **43**, 181
[77] Thorstensen, T. C. and Theis, E. R., ibid., 1949, **44**, 841
[78] Chambard, P., *Bull. Ass. franç. Chim. Ind. Cuir.*, 1947, **9**, 157
[79] Gelle, M., ibid., 65
[80] Somerville, I. C. and Rau, W. J., *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 784
[81] Patterson, G. H. and Jurney, R. C., ibid., 2, 14
[82] BIOS Final Reports Nos. 150, 762, 861, 1164, 1425
[83] Reed, C. F., U.S.P. 2,046,090

[84] Kanagy, J. R. and Harris, M., *J. Res. Nat. Bur. Stand.*, 1936, **14**, 563
[85] Gurin, S. and Clarke, H. T., *J. biol. chem.*, 1934, **107**, 395
[86] Stather, F. *et al.*, *Collegium*, 1941, **859**, 297, via *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 236
[87] Herfeld, H. and Schubert, R., ibid., 1942, **870**, 337, via *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 756
[88] Marshall, F. F. and Turley, H. G., *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 870
[89] Hough, A. T., *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 114
[90] Kulberg, L. M. and Chechenov, N. I., *Zavodskaya Lab.*, 1948, **14**, 790; *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 118
[91] Jany, J., *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 665
[92] Lattey, W. J., *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 244
[93] Kubelka, V., *Tech. Hildka Koz.*, 1949, **24**; *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 823
[94] Adams, R. S., and Merrill, H. B., *J. Amer. Leath. Chem. Ass.*, 636
[95] Lollar, R. M. and O'Flaherty, F., ibid., 22
[96] Browning, B. L. *et al.*, ibid., 30
[97] Mathews, L. M. *et al.*, ibid., 459
[98] Haglund, A., ibid., 68
[99] Salvesen, J. R. and Hogan, D., *Analyt. Chem.*, 1948, **20**, 909
[100] Kubelka, V. and Kubeckova, E., *Tech. Hlidka Koz.*, 1948, **23**, 105, 210
[101] Kubelka, V., ibid., 295
[102] Kubelka, V. *et al.*, ibid., 333
[103] Kuntzel, A. and Bosse, R., *Colloquiumsber. Inst. Gerbereochemie Tech. Hockschule, Darmstadt*, 1947, **1**, 59
[104] Kuntzel, A., ibid., **3**, 18
[105] Hiller, A. *et al.*, *J. biol. Chem.*, 1948, **176**, 1401
[106] Kubelka, V., *Tech. Hlidka Koz.*, 1948, **23**, 117
[107] Hindin, S. G. and Grosse, A. V., *Analyt. Chem.*, 1948, **20**, 1019
[108] McComb, E. A., ibid., 1219
[109] Kremen, S. S., *J. Amer. Leather Chem. Ass.*, 1949, **44**, 774
[110] Ibid., 631
[111] Kubelka, V., *Tech. Hlidka Koz.*, 1948, **23**, 91
[112] Shome, S. C., *Analyt. Chem.*, 1948, **20**, 1205
[113] Nieuwenberg, C. J. van and Unterbroek, G., *Analyt. Chim. Acta*, 1948, **2**, 88, via *J. Amer. Leath. Chem. Ass.*, 1949, 417
[114] Wolstenholme, S., *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 116
[115] Willard, H. H. and Hahn, R. B., *Analyt. Chem.*, 1949, **21**, 293
[116] Kubelka, V. *et al.*, *Tech. Hlidka Koz.*, 1948, **23**, 261
[117] Proposal of A.L.C.A. Tannin Analysis Committee, *J. Amer. Leath. Chem. Ass.* 1948, **43**, 657
[118] Cheronis, N. D. *et al.*, ibid., 1949, **44**, 282
[119] Hough, A. T., *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 164
[120] Oehler, R. and Kilduff, T. J., *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 151
[121] Highberger, J. H. *et al.*, ibid., 1948, **43**, 307
[122] Hough, A. T., *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 284
[123] Noerr, H. and Hees, W., *Coll. Inst. Gerb., Darmstadt*, 1948, **2**, 3
[124] Mitton, R. G., *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 100
[125] Roddy, W. T. *et al.*, *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 308
[126] Faibishenko, M. A., *Leg. Prom.*, 1948, **12**, 13; *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 308
[127] Mitton, R. G., *J. Soc. Leath. Tr. Chem.*, 1948, **32**, 405
[128] Mitton, R. G., ibid., 1949, **33**, 85
[129] Kubelka, V., *Tech. Hlidka Koz.*, 1948, **23**, 66, 88
[130] Compton, L. D., *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 140
[131] Highberger, J. H., ibid., 1947, **42**, 493
[132] Gustavon, K. H., ibid., 1948, **43**, 741
[133] Weir, C. E., ibid., 1949, **44**, 79
[134] Shaw, K. W. and Maeser, M., ibid., 796
[135] Kuntzel, A., *Stiasny Festschrift*, 1937, 191
[136] Musgrave, A. J., *Ann. app. Biol.*, 1947, **34**, 449
[137] Robertson, M. E. and Haines, B. M., ibid., 457

[138] Anderson, H., *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 250
[139] Moore, M. H., *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 326
[140] Gustavson, K. H., ibid., 392
[141] Vleck, A. K. and Mansfeld, V., *Collegium*, 1942, **862**, 41 ; *J. Amer. Leath Chem. Ass.* 1949, **44**. 348
[142] *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 238
[143] Hagen, O., *Ledertech. Rundschau.*, 1949, **2**, 1 ; *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 389
[144] Ames, J., *J. Soc. Leath. Tr. Chem.*, 1949, **33**, 407
[145] Nito, H., *J. agr. Chem. Ind. Japan*, 1944, **20**, 453 ; *Chem. Abstr.* 1948, **43**, 1206
[146] Kenyon, J. and Silberstein, V., U.S.P. 2,456,630
[147] Chadray, M. A., Indian Pat. 35,519 ; *J. Amer. Leath. Chem. Ass.*, 1949, 422
[148] Damschroder, R. E. and Kaufman, M. E., U.S.P. 2,460,809 ; *J. Amer. Leath. Chem. Ass.*, 1949, **44**, 525
[149] Ferry, J. D. and Eldridge, J. E., *J. phys. colloid. Chem.*, 1949, **53**, 184

AGRICULTURE AND HORTICULTURE

BY MEMBERS OF THE AGRICULTURE GROUP

INTRODUCTION (A. G. Pollard)

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THE literature considered in this year's Report is again predominantly utilitarian rather than academic. The major world problem of stepping-up food production is no less intense or urgent, but the approach to the problem is perhaps calmer and possibly more forceful. Results of agricultural investigations have circulated much more freely during the year although there is still a mass of foreign literature which is not generally available. Readily accessible publications, too, must inevitably contain information actually obtained during the war years, but now being reported for the first time. Under these circumstances and with due consideration of space limitations, this Report aims at dealing with a number of current agricultural topics without necessarily limiting its attention to reports actually published during the year under review: it is in no sense an exhaustive account of the 1949 literature.

The production of adequate supplies of fertilizers remains a primary problem in the general drive towards meeting the world's ever-increasing food requirements. New processes for the manufacture of phosphatic fertilizers from rock phosphate form the subject of many investigations. The importance of the physical condition of fertilizers, as an economic and practical factor, is demonstrated by the continued interest in granulation, conditioning, etc. The generally insufficient supply of potassic fertilizers is probably one important reason for the recently intensified investigations of the mechanism of the process of 'fixation' of potassium in soils. A better understanding of this phenomenon may have an important bearing on the economic use of potash fertilizers and may well introduce a new conception of the controversial subject of the availability of these fertilizers.

Among the important potash-consuming crops the potato still occupies a pre-eminent position here and in other countries. Investigations of many aspects of the cultivation, manuring, protection against pests and diseases and storage of potatoes have been numerous recently and demand consideration in this Report. The significance of trace elements in plant nutrition continues to attract the attention of numerous research workers, particularly those concerned with the more intensive cultivation of horticultural subjects. As has been the practice in these Reports for some years an up-to-date review of the literature concerning several of these secondary nutrients is presented. The quality of crops, and especially of food crops, in relation to conditions of cultivation offers a wide and responsive field for research. Some of the more important among the numerous investigations of the amount and distribution of vitamins in food crops fall to be considered this year.

In connexion with the feeding of farm animals the supply or substitution of protein foods has necessarily been a matter of vital importance in recent years. Experiments relating to the utilization of protein hydrolysates and of urea in the animal system have added considerably to our knowledge of the nitrogen nutrition and metabolism of animals and may lead, ultimately, to some economy in the practical use of the costly protein feeding-stuffs. The effects of feeding iodinated proteins to dairy cattle and other livestock has recently provided much interest for both dairy experts and physiologists and some account has been included here of the progess of these investigations in the past two or three years. Relationships between the copper nutrition of sheep and the production and character of the wool also calls for comment.

Recent developments in the production of synthetic fungicides have been extensive and of great interest. Space limitations prevent more than a short reference to some of these substances here ; it is unavoidable that fuller consideration of this subject must be deferred for a later Report. Similarly the subject of the control of plant nematodes must on this occasion be limited almost entirely to considerations of the use and properties of that somewhat versatile material 'DD.'

In analytical matters the current literature has been concerned more with the improvement and adaptation of known methods than with the development of new ones. Much interest is maintained in the vexed question of the measurement of availability of nutrients in soils and fertilizers, especially in that of phosphate in fertilizers. The demand for official re-consideration of the question of phosphate availability is still widespread. The development of the new synthetic insecticides and fungicides has brought the need for a variety of new analytical methods. Among those noted in the present Report are methods for 'parathion' and 'Spergon.'

(For the general Report on insecticides see the chapter 'Control of Pests,' p. 649.)

SOILS (A. H. Cornfield)

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Potash fixation and release

This survey covers the work which has been published during the last few years on the problems of the fixation of potassium by soils and the conversion of non-exchangeable and water-insoluble forms of potassium into forms which are available to plants. Fixed potassium is still generally regarded as that potassium which cannot be extracted by reagents used for displacing exchangeable bases from the soil.

Joffe and Levine[1] found that potassium which had been fixed by alternate wetting and drying was resistant to the action of hot hydrochloric acid of up to 0·1N. concentration, whereas hot 0·5N-hydrochloric acid released about 15% of the fixed potassium. Hoover[8] found that moist storage of a montmorillonitic soil to which increasing amounts of potassium had been added resulted in increasing amounts of potassium being

fixed. With a kaolinitic soil potassium was fixed only from the highest rate of application (400 p.p.m.). Where fixation occurred more potassium was fixed from potassium chloride than from an equivalent amount of potassium dihydrogen phosphate. Joffe and Levine[3] also found that the associated anion affected the amount of fixation by showing that a hydrogen-bentonite fixed more potassium when it was added as acetate than when it was added as chloride.

Joffe and Levine[1–5] studied the fixation of potassium in relation to the exchange capacity of soils. They found that when cation exchange was facilitated, e.g. by carrying out the process in alcoholic instead of aqueous solution, or when the exchange capacity of the system was increased, e.g. by grinding pyrophyllite or bentonite, there was an increase in the amount of potassium fixed. Alternatively when the exchange capacity of a soil was reduced by treatment with ferric chloride solution, or when exchange positions were blocked with other cations, potassium fixation was reduced. They found a simple linear relationship between the amount of potassium entering the exchange complex and the amount of potassium fixed. They concluded from these and other experiments that before potassium can be fixed it must be in the exchangeable state. They also showed that the increase in fixation which generally follows liming is due not to the increased amount of calcium present but to the increase in the p_H of the system and the consequent effect on the percentage base saturation of the exchange complex ; since potassium displaces calcium more readily than it displaces hydrogen, more potassium enters the exchange complex and therefore more potassium is fixed.

Truog and Jones[7] and Joffe and Kolodny[6] found that fixation of potassium resulted in a decrease in the exchange capacity of the fixed system. Whereas Truog and Jones found for both a number of soils and a number of minerals that the decrease in exchange capacity was approximately equivalent to the amount of potassium fixed, Joffe and Kolodny found no equivalence between the two values.

A number of theories have been put forward to explain the mechanism of potassium fixation. Joffe and Levine,[5] Truog and Jones,[7] and Page and Baver[18] suggest that potassium is fixed between the layers of the layer-lattice minerals. Volk[10] found that muscovites which were more deficient in potassium were able to fix more potassium than those which had more nearly their theoretical quantity of potassium. Soils containing layer-lattice minerals of the montmorillonite group and hydrous micas were able to fix more potassium than those containing kaolinitic minerals only[5,11,12,19] Page and Baver[18] suggest that the reason why large ions such as diethylamine can reduce the amount of potassium fixed by drying is because they prevent the sheets of the minerals from contracting during the drying process. Univalent and bivalent cations with ionic sizes similar to the size of certain free spaces within the lattice were closely correlated with susceptibility to fixation. With regard to the fixation of other cations, Joffe and Levine[2,21] found that barium, strontium, calcium, magnesium, and sodium are not fixed but that ammonium is fixed, thus confirming results obtained by Chaminade.[22] It is interesting to note that, whereas ammonium fixation is hardly affected by an equal amount of potassium, the presence of ammonium depresses sharply the amount of

potassium fixed.[3] Martin, Overstreet, and Hoagland[16] consider that fixation first involves an exchange adsorption of cations and then a fixation which results in a reduction in the total exchangeable cations of the soil. It is assumed that fixation depends on the presence of a limited number of attraction spots that possess special properties either because of their position in the clay lattice or because of the nature of the soil minerals with which they are associated. They maintain that the process does not depend on the presence of clay minerals of the layer lattice type.

The effect of organic matter on potassium fixation continues to receive attention. Gourley and Wander[14] and Walker and Sturgis[15] showed in field experiments that organic matter depressed the amount of potassium fixed. Joffe and Levine[3] consider that the reason for depression of fixation by organic matter is that it competes with the mineral matter for exchangeable potassium. Martin, Overstreet, and Hoagland[16] concluded that the humus in soils does not fix potassium, but Hurwitz and Batchelor[17] report a biological fixation of up to 200 lb. per acre of potassium when plants residues were added to soils ; no relation was found between the extent of fixation and the carbon/nitrogen ratio. Pchelkin,[13] on the other hand, found that when the humus of mineral soils was destroyed by oxidation their fixing power was reduced. Worsham and Sturgis[20] found that the addition of organic matter to soils markedly increased the available potassium of both acidic and basic soils.

A number of workers have shown that the non-exchangeable forms of potassium are available to plants. Attoe and Truog[23] found in pot tests that maize and oats were able to make considerable growth on soils from which all exchangeable potassium had been removed, whilst Olsen and Shaw[24] obtained similar results using Neubauer seedling tests on the silt fractions of soils which had been leached free of exchangeable potassium. They found that the amounts of non-exchangeable potassium taken up by the rye seedlings increased with decreasing silt particle size. Chandler, Peech and Chang[25] found upon continuous cropping of soils with successive crops of clover that the exchangeable potassium content decreased very rapidly at first and then more gradually until a certain level was reached, when the potassium supplying power of the soil was determined largely by the rate at which the non-exchangeable forms of potassium were converted to the exchangeable form. In spite of the ability of clover to take up large amounts of non-exchangeable potassium, they concluded that the yield of clover was closely associated with the amount of potassium present in the exchangeable form. Bear, Prince and Malcolm[26] came to the same conclusion, even though they reported that twenty soils of varying texture were able to supply to plants considerably different amounts of non-exchangeable potassium. Walsh and Cullinan[31] found that the potassium which had been fixed by alternate wetting and drying of a number of soils was only partially available to a first crop of mustard, as shown by severe potassium-deficiency symptoms, but that further crops were able to draw on supplies of fixed potassium.

Different plants are capable of utilizing different amounts of non-exchangeable potassium. Evans and Attoe[32] found that Ladino clover removed from 1·2 to 1·7 times as much non-exchangeable potassium as did oats from soils high in exchangeable potassium, but that equal

amounts of non-exchangeable potassium was removed by the two plants from soils low in exchangeable potassium. Lewis and Eisenmenger[33] found in general that seed plants of the lower order of development were capable of utilizing much more soluble and insoluble potassium, the latter being supplied by orthoclase feldspar, than were plants of a high order of development.

Because of the ability of plants to absorb non-exchangeable forms of potassium Schachtschabel[27] points out that chemial methods of determining availability which rely on the extraction of the exchangeable potassium only cannot always be considered good indicators of the potassium supplying power of soils. He considers that biological methods of assessing availability, such as the Neubauer seedling method, should be continued to be used in order to obtain reliable results. Reagents capable of dissolving both exchangeable forms of potassium and also part of the non-exchangeable forms have been suggested as giving better indications of availability. DeTurk, Wood and Bray,[28,29] for instance, found that the potassium which was dissolved by boiling soils for 10 minutes with N-nitric acid was directly related to the potassium-supplying power of the soils; Attoe and Truog[30] found that non-exchangeable potassium which was dissolved by extraction of the soil for 1 hr. with 0·5N- or N-hydrochloric acid was moderately available to plants.

The fixation of potassium in non-exchangeable forms is not always regarded as an undesirable process. DeTurk, Wood and Bray[28,29] consider that fixation is desirable, since fixed potassium is not lost by leaching, and in any case becomes available to crops on depletion of the more available forms; Evans and Attoe[32] consider that the process is beneficial because it conserves potassium when present in relatively large amounts by retarding or preventing luxury consumption.

Erosion

A number of workers have recently reported the results of tests on the movement of soils due to rainfall under controlled conditions. Ekern and Muckenhirn[34] studied the transport of sand down varying slopes by artificial rainfall in which the quantity and size of the water droplets could be controlled. With constant drop size and time the amount of sand transported was directly proportional to the intensity of precipitation. The relation between the percentage slope and the fraction moved down the slope was given by the equation

$$\% \text{ transported} = 50 + 0{\cdot}94 \text{ slope } \%$$

and the relation between drop diameter (mm.) and amount (tons/acre) transported in a 5-min. period with a precipitation intensity of 1 in./hr. was

$$\text{Transport} = 9{\cdot}25 \log \text{diam.} - 2{\cdot}73.$$

Woodburn,[35] in a study of the amount of soil lost by splash erosion with artificial rainfall, found that curves of the type $S = KE^p$ fitted the data quite well, where S was the amount of soil splashed, E the applied energy expressed as the time during which the rain fell, and K and p were

constants depending on the soil. It was found that splashing from pulverized soils was much greater than from undisturbed soils, and that the splash rate fell when the rainfall was prolonged.

Ellison[38] points out that work on the removal of soil particles by surface flow awaits the development of a standard 'soil' of properties such that the abrasive characteristics of the flow will remain unaltered by materials detached from it. Ellison and Ellison[36] found that in the early stages of erosion, when run-off moves as a broad sheet, the soil-suspending capacity of the run-off is low but the impact of raindrops causes sufficient turbulence greatly to increase the amount of soil suspended and therefore lost by erosion. If the soil surface is fully protected against the impact of raindrops very little soil will be transported. Harold[37] found for an area in which the sealing of surface soil by rain was serious and consequently the run-off was high, that the application of lime and fertilizers alone or the introduction of lucerne into a maize–wheat rotation had little effect in preventing the trouble. Mulching improved conditions rapidly and the introduction of two years of grass in the rotation was also quite effective.

The deleterious effect of burning the vegetation on soils continues to be pointed out. Rowe[39] found that the annual burning of the vegetation of woodland for 9 years resulted in an average annual run-off of 14% of the precipitation, loss by erosion of 25,000 lb. of soil per acre, and a reduction in infiltration capacity of 70–95%, as compared with unburned plots which retained all rainfall and lost only 1·5 lb. of soil per acre. Rycroft[40] found that during the winter following the autumnal burning of veldt vegetation there was a highly significant increase in the rate and volume of stormflow of the catchment stream, a rise in flood heights, and an increase in stream discharge; McKay and Baker[41] found that the amount of soil lost by erosion was 3–4 times greater where plant residues had been burnt and either turned in or left on the surface than when unburnt residues had been similarly treated.

References

[1] Joffe, J. S. and Levine, A. K., *Soil Sci.*, 1946, **62**, 411
[2] Ibid., 1947, **63**, 151
[3] Ibid., 241
[4] Ibid., 329
[5] Ibid., 407
[6] Joffe, J. S. and Kolodny, L., *Soil Sci. Soc. Amer. Proc.*, 1938 (1937), **3**, 107
[7] Truog, E. and Jones, R. J., *Ind. Eng. Chem.*, 1938, **30**, 882
[8] Hoover, C. D., *J. Amer. Soc. Agron.*, 1944, **36**, 1003
[9] Wood, L. K. and DeTurk, E. E., *Soil Sci. Soc. Amer. Proc.*, 1943 (1942), **7**, 148
[10] Volk, G. W., *Soil Sci.*, 1938, **45**, 263
[11] Jacob, A., *Bodenk. Pfl. Ernähr.*, 1940, **21/22**, 621
[12] Alexander, L. T., Hendricks, S. B. and Nelson, R. A., *Soil Sci.*, 1939, **48**, 273
[13] Pchelkin, V. U., *Pedology*, 1946, 604
[14] Gourley, J. H. and Wander, I. W., *J. Amer. Soc. Agron.*, 1939, **31**, 590
[15] Walker, R. K. and Sturgis, M. B., *Ass. S. Agr. Workers Proc.*, 1940, **41**, 79
[16] Martin, J. C., Overstreet, R. and Hoagland, D. R., *Soil Sci. Soc. Amer. Proc.*, 1946, (1945), **10**, 94
[17] Hurwitz, C. and Batchelor, H. W., *Soil Sci.*, 1943, **56**, 371
[18] Page, J. B. and Baver, L. D., *Soil Scil Soc. Amer. Proc.*, 1939 (1938), **4**, 150
[19] Seatz, L. F. and Winters, E., ibid., 1943 (1942), **8**, 150
[20] Worsham, W. E. and Sturgis, M. B., ibid., 1941 (1940), **6**, 342
[21] Joffe, J. S. and Levine, A. K., ibid., 1939 (1938), **4**, 157

[22] Chaminade, R., *C.R. Acad. Sci., Paris*, 1940, **210**, 264
[23] Attoe, O. J. and Truog, E., *J. Amer. Soc. Agron.*, 1944, **36**, 1009
[24] Olsen, S. R. and Shaw, B. T., ibid., 1943, **35**, 1
[25] Chandler, junr., R. F., Peech, M. and Chang, C. W., ibid., 1943, **37**, 709
[26] Bear, F. E., Prince, A. L. and Malcolm, J. L., *Soil Sci.*, 1944, **58**, 139
[27] Schachtschabel, P., *Bodenk. Pfl. Ernähr.*, 1941, **24**, 371
[28] DeTurk, E. E., Wood, L. K. and Bray, R. H., *Soil Sci.*, 1943, **55**, 1
[29] Wood, L. K. and DeTurk, E. E., *Soil Sci. Soc. Amer. Proc.*, 1941 (1940), **5**, 152
[30] Attoe, O. J. and Truog, E., ibid., 1946 (1945), **10**, 81
[31] Walsh, T. and Cullinan, S. J., *Emp. J. exp. Agric.*, 1945, **13**, 203
[32] Evans, C. E. and Attoe, O. J., *Soil Sci.*, 1948, **66**, 323
[33] Lewis, C. C. and Eisenmenger, W. S., ibid., **65**, 495
[34] Ekern, R. C. and Muckenhirn, R. J., *Soil Sci. Soc. Amer. Proc.*, 1948 (1947), **12**, 441
[35] Woodburn, R., *Agric. Engng*, 1948, **29**, 154
[36] Ellison, W. O. and Ellison, O. T., ibid., 1947, **28**, 442
[37] Harold, L. L., ibid., 563
[38] Ellison, W. B., *Trans. Amer. geophys. Un.*, 1948, **29**, 499
[39] Rowe, P. B., Calif. Dept. Nat. Resources, Div. Forestry, 1948
[40] Rycroft, H. B., *J. S. Afric. Forestry Ass.*, 1947, **15**, 80
[41] McKay, H. C. and Baker, G. O., *Soil Sci. Soc. Amer. Proc.*, 1947 (1946), **11**, 553

FERTILIZERS (D. P. Hopkins)

Consultant on Fertilizers

Manufacture

It can be said, and certainly for the first time since 1940, that manufacturing capacity is drawing closer to the demand. But this is not a matter for complacency or rejoicing, but merely indicates a tendency, dictated by artificial farm economics, for demand to stabilize at a figure considerably below that quantity which even the most prudent agricultural scientists would regard as nationally desirable. This matter of the amounts of fertilizer which should be manufactured and used will be referred to in another section of this Report, but here it is necessary to point out that manufacturers reached the end of 1949 with less confident hopes of continuing expansion despite calls for considerably increased fertilizer consumption. In America and Britain the old and limiting influence of the farmer's purchasing power is again beginning to count more powerfully than scientific argument. In the United Kingdom the official announcement that fertilizer subsidies would be withdrawn in a two-stage process in 1950 and 1951 was a disturbing complication; the consequent rises in price of most fertilizers will not be small and some recession in consumption is possible.

Several papers on granulation have been published. Steventon and Sherwin[1] have surveyed the history of this development from the Oberphos process to the present-day pre-mix, wetting and drying process now used by most manufacturers. Original hopes that fertilizers could by this method be mixed and bagged in a continuous process would seem to have been falsified. A 'maturing' or 'set-repressing' period in the heap is required before bagging can take place; this would seem, at any rate, to be the experience reported by some manufacturers. The setting tendency

of granules requires fundamental rather than large-scale 'trial-and-error' investigation. Another problem of granulation is the variation in analysis between rejected fines and granules. Procter[2] has very fully described the slurry dispersion method of granulating superphosphate and superphosphate-containing mixtures. In this method the mixing of finely divided superphosphate or other materials with a slurry of superphosphate in a rotating conditioner produces rapidly formed granules; its potential advantage is that reactions inherent in superphosphate manufacture are utilized in the process of granulation. More uniformly sized and composed granules are producible by this process. It is possible, however, that the degree of water-soluble conversion of phosphate is reduced. Development work has been handicapped by frequent changes in rock-phosphate quality during the war years, and it is still too early to assess the true possibilities of this process.

The 'Super Flo' process for continuous superphosphate manufacture has been described in an American paper.[3] The rock-acid reaction is carried out in a tower, the rock entering as a fine dust stream and the acid as a spray. Interaction is rapid and a product of hard grain structure is obtained. Three men are said to be able to operate a 45-ton/hr. plant; also, such plants (two of which are now in operation in the United States) can be started up or stopped in a few minutes, an important advantage if conditions of fluctuating demand return. Detailed account has been given of well established Canadian processes[4] for producing phosphoric acid and ammonium phosphate from phosphate rock. Another useful paper from across the Atlantic is Whitney and Hollingsworth's short description of defluorinating rock phosphate by thermal treatment in the presence of silica and steam but without fusion; the product contains about 20% of P_2O_5 and 0·1% or less of F, and is effective as both feeding-stuff and fertilizer.[5]

Two papers have dealt with sulphate of ammonia, each with special attention to crystal shape and size. The British paper by Ettle[6] describes chemical methods of influencing the crystalline form in which synthetic sulphate of ammonia is finally produced; he also discusses the greater difficulty of modifying by-product sulphate of ammonia crystals owing to their 'natural' content of influential ions as impurities, e.g. iron. An earlier American survey[7] is less detailed but shows a different approach to conditioning based upon dryness, neutrality, and strict control of size of crystal.

Possibly the most interesting development about the third fertilizer nutrient—potash—was the strong recommendation, made by the Mineral Development Committee,[8] that potash deposits in Yorkshire should be more fully investigated. The potash salt bed, which was found at a depth of about 4000 ft., is believed to be a part of an extensive deposit stretching from North Germany to North-East England. Brine-pumping rather than normal salt-mining methods were suggested; but, in establishing a second exploratory bore-hole in 1948 to investigate this possibility, more encouraging evidence for recovering solid sylvinite (about 34% KCl) was obtained. The official report observes that although 'it may be as long as two years before sufficient additional exploration has been carried out, it looks as if the prospect is emerging of a most important addition

to the country's natural reserves.' In this connexion it is not irrelevant to take note of French plans for her fertilizer industry, which envisage a reduced tonnage of potash for export and a greater use of potash upon her own soils.[9]

Although much more than 50% of British compound fertilizers are now granulated, attention was paid in 1949 to the problem of conditioning the powder-type mixture, and investigations by the Chemical Research Laboratory (D.S.I.R.) on the use of sawdust as a conditioner were published and discussed.[10] Other bulky organic conditioners were also investigated, e.g. leather dust, peat, seaweed, etc. The symposium of papers should be studied in its entirety as there is evidence of disagreement with the claim that very small percentages of sawdust significantly reduce the extent of setting. More fundamental chemical studies of the setting phenomenon have been reported from the United States[11]; the set is attributed to the formation of complexes of alkali and alkaline earth anions with SO_4 and PO_4 cations, and the completeness to which these formations take place during curing is influenced by the amount of moisture present. The new compounds formed can be less hygroscopic than the initially-mixed materials. In approaching the problem of hardening of fertilizers it is important to distinguish between the chemical event of 'setting' and the more physical event of 'caking.' It has been indicated in a survey of future American research using radioactive isotope tracers that the complex compounds formed in mixed fertilizers will be studied by these new methods.[12]

An important British decision in 1949 was that of the fertilizer industry to form a Research Association under the Industrial Research Association schemes of the Department of Scientific and Industrial Research.[13] Although a number of centres exist for the study of fertilizer use, no general centre is to-day concerned with problems of manufacture. One of the most pressing problems, viz. the shortage and rising cost of sulphuric acid for rock-phosphate treatment, was discussed in the 1948 Report. E. P. Hudson, in advocating the formation of the proposed association, referred to the easing of this national and industrial problem as one of the most urgent tasks for research. This changing economic aspect of the superphosphate industry was mentioned in last year's Report. Problems of this nature will become more pressing as real prices for fertilizers take the place of subsidized prices. In this connexion a recent F.A.O. publication[14] has outlined the schemes by which farmers of various countries receive financial or credit assistance in their fertilizer purchases; but one wonders how many of these systems of assistance are only temporary and already being reduced or discarded as supposed economies. Soil scientists have always urged that fertilizers must be 'cheap' but no time has been less favourable than is the present for laying the entire responsibility of providing 'cheapness' upon manufacturers. The final words of the F.A.O. book are worth quoting:

> 'One of the strongest links in the chain of successful crop production is the efficient use of fertilizers. The farmer himself has to forge it, but he needs technical guidance and, under some conditions, economic assistance if this link is to be strongly made.'

Can any country which has to import food afford to discourage the use of fertilizers upon such soils as it possesses? To do so would seem to be the falsest of economies.

To what extent can manufacturers provide cheapness? Crowther has drawn attention to the decline of sulphate of ammonia and the rise of ammonia and 'nitrogen' solutions in the United States.[15] 1946 figures show that ammonia solutions provided N at 5·2 cents per lb. as compared with 7·1 cents for N from sulphate of ammonia, notwithstanding the fact that since 1900 the economic effect of synthetic fixation processes has approximately halved the price of sulphate of ammonia. Crowther points out that 'over half of the nitrogen fertilizer sold in the United States leaves the nitrogen factory in forms requiring, for their manufacture, no other raw materials than air, water and coal.' The introduction of such practices in this country is in any case greatly inhibited by the legal necessity to regard water-soluble phosphate as the superior form of that plant-food; alkaline nitrogenous materials cannot be mixed with water-soluble phosphate without transformation of the phosphate. As an instrument of commercial justice the 1926 Fertilizers and Feeding Stuffs Act may have been necessary, but it is strongly held in many quarters that the Act has long passed the age when it should have been replaced by a younger piece of legislation in which some of the technical developments of the past quarter-century are recognized. Indeed, it is possible that new conceptions of fertilizer-controlling legislation could be introduced. The limits of analytical variation which are at present allowed to manufacturers are much smaller than the variations which could be detected by field results. It may well be asked whether it is truly economic to work to standards of accuracy not actually required for the final purpose of the product. In a recent paper (which at the time of reporting has appeared only in digested form)[16] Crowther stated that no field tests showing significant differences for 16% or 18% superphosphate were known, and he tentatively suggested that regulations might pay more attention to declarations of materials used and less to statements of plant-food 'strength.' After so many years of a converse legislative policy, such a view is certain to be regarded as revolutionary but it is in fruitful harmony with both modern soil science and current economic problems of fertilizer production.

The intrusion of the radio-isotope method of research into fertilizer study is more appropriately dealt with in another section, but one paper dealing with the preparation of 'isotope-labelled' fertilizer materials should be referred to here.[17] The production of about 7 cwt. of radioactive phosphatic fertilizers in five different forms for a number of field experiments in 1948 is fully described, diagrammatic flow-charts being given for each product.

Use of fertilizers

Caution and uncertainty on the part of manufacturers of fertilizers has been evident in 1949; but an almost paradoxical contrast is found when we turn to their use. Notable among a number of exhortations to use more fertilizer was the First Report of the Committee on Industrial

Productivity[18]; the under-use of nitrogenous fertilizers upon grassland was strongly criticized.

> 'Today less than a quarter of the 18 million acres of grassland in the United Kingdom receives dressings of nitrogenous fertilizer, in contrast with the very much higher proportions for cereals and root crops—in spite of the fact that experimental work has shown that the response to a given quantity of nitrogen is greater in the case of grass than for either cereals or root crops. . . . We must emphasize that, in our view, unless adequate supplies of fertilizer become available, the agricultural target cannot be attained, and the full benefits of the expansion programme will be lost.'

The urgent provision of additional capacity for manufacturing nitrogenous fertilizer was recommended. Nevertheless, by the end of 1949 there were clear signs that the amount of nitrogenous fertilizer available was reasonably meeting the demand. This indicates that a vast amount of educational work must be carried out before farmers generally share the convictions of the Committee about nitrogen and grassland; the exceptionally dry spring and summer of 1949 did not help official agricultural advisers.

Later Sir John Russell's Presidential Address to the British Association paid a good deal of attention to the world role of fertilizers.[19] Use of fertilizers was one of the chief methods of intensifying food production per acre, and modern Malthusianism was to find its most hopeful answer in the more intensive cultivation of land already in use. In particular the rice crop of Asia offered vast scope for fertilizer use. Russell drew attention to the Japanese application of Pearsall's studies of oxidation and reduction layers in Cumberland marshland, the results of which had given a new scientific basis for the fertilization of a swamp-crop like rice. Sulphate of ammonia could be safely pushed down into the lower reduction layers and would remain available for plant needs; nitrates could be used in the oxidation upper zones as immediate top-dressings during rapid growth. Of parts of the world which already can be looked upon as fertilizer-conscious, Russell said 'much more fertilizer could advantageously be used if farmers' means permitted.'

A more detailed account of the possible extensions of the use of fertilizers has been given in the F.A.O. publication previously mentioned.[14] What is known of the basic principles of fertilizer use is admirably summarized and explained to help agricultural administrators and advisers all over the world to apply these principles to their own local conditions and cropping systems. It is to be hoped that the book will have the widest possible distribution.

There have been several papers dealing with the somewhat related subjects of placement and phosphate fixation. Stewart[20] has reviewed results of contact-placement with cereals; compared with broadcast application, such dressings are more efficient, but little difference is shown for nitrogen. Spectacular rises in efficiency had been shown by combine-drilling potassic fertilizers on certain badly K-deficient soils. Cooke has contributed two wide surveys of placement development[21,22] and also a paper on placement apparatus.[23] It might be commented that the

demands for perfection of fertilizer condition made by placement machinery cannot be pushed too far; the materials which must mainly provide the world's plant-foods do not happen to possess unlimited flexibility of physical properties, and although conditioning modifications are in some cases possible there is an economic limit to the amount of processing that can be given. A machine whose effective performance depends upon the fertilizer being in an unusually dry condition is not necessarily a progressive and practical innovation. Williams[24] has provided a general study of phosphate fixation, the main conclusion of which is that fixation is least severe at a p_H of 6·5; adequate liming and placement are the principal measures for reducing wastage. A somewhat shorter survey[25] has suggested that the actual significance of fixation will be more accurately estimated when more results from research with radio-isotope ^{32}P are to hand; also, that the physiological study of the plant as a phosphate-assimilator may be quite as important an approach as the chemical study of soil and fertilizer interactions.

Nitrogen test-results reported by Holmes[26] probably form the chief evidence which influenced the Committee on Industrial Productivity (*see above*). He showed that the response to 'nitro-chalk' with grassland was high and progressive up to as much as 18 cwt. per acre. Protein outputs were raised by 200% to 240% with the higher rates of dressing and by spacing the applications fairly steady protein production was secured throughout the April–October period—an important aspect of grass growth for silage or drying. As has been known for at least 20 years, the full effect of nitrogen treatments upon grass cannot be assessed by crop-weight increases alone; the protein content of the grass is more sharply increased. It might be wise to interpret these tests results with conservatism; certainly much more investigation and experience are needed before such huge dressings could be widely recommended. They do show, however, that the present and almost meaningless statistical figure of 0·1 to 0·2 cwt. of sulphate of ammonia now used on our grassland could be greatly increased with safety and profit. Should grass whose protein content has been so highly 'forced' by nitrogen fertilization be directly grazed by cattle? A recent article from New Zealand[27] provides evidence from veterinary investigations that incidence of milk-fever, acidosis, and grass staggers was most noticeable on farms where large dressings of fertilizers had been given to the pastures. This finding was based upon a survey of 700 dairy farms covering about 50,000 cows. The conclusion reached was not one that condemned the use of fertilizers; the liberal addition of molasses to the diet to make good the imbalance between protein and carbohydrates was recommended.

Many more papers based upon the use of radio-isotopic phosphorus have appeared in 1949. An outstanding event was the publication of a collected series from different experimental centres in the United States; and this single reference actually covers 12 papers.[28] The utilization of P by different crops on various types of soil, the effect of placement of fertilizer upon utilization, and the supply-efficiencies of different fertilizer forms were all studied. The P efficiency of animal and green manures was also investigated. Two fairly general conclusions were that the selective demand for fertilizer P is much greater in early stages of growth,

and that superphosphate was the most efficient of the P fertilizers tested for most crops. The percentages of fertilizer P finally recovered by crops were generally low, considerably lower in many cases than 'pre-isotope' estimates of 15% to 20%. This is in line with Canadian evidence discussed in last year's Report. It would seem now to be fairly well established that the early uptake of fertilizer P enables plants to assimilate more soil P later; previously this additional total P taken up has been attributed to the fertilizer source. There is a limitation to the usefulness of radio-isotopic P as a tool for measuring fertilizer efficiencies; its half-life is relatively short and the radiation-emitting 'label' can at the longest last only for a short growing season; the residual values of various P fertilizers cannot, therefore, be compared, and, as is well known, the merits of some P fertilizers are based upon long-term considerations. The isotope method of inquiry seems better fitted to probe the mechanism of nutrient assimilation by the growing crop than to assess the values of phosphatic materials in the soil. However, this is not a serious limitation for at the present time the greatest gap in our knowledge about phosphorus as a plant-food is our almost total ignorance of the details of assimilation.

Bear[29] has discussed the ever-present and ever-artificial 'humus *versus* fertilizer' controversy, and provided more evidence to defeat the extremists on their own ground. A result quoted showed that 15 years of continuous NPK fertilizer treatment raised the organic matter content of a soil by nearly 50%. Two surveys—by Wallace[30] and by Gilbert[31]—of the trace nutrients in general have appeared. Wallace deals with the needs of horticultural plants and Gilbert discusses the pros and cons of fortifying commercial fertilizers with trace nutrients. It is impossible to select examples from the many papers which have dealt with individual trace nutrients for often enough their case histories have only local or regional significance. It would appear, however, that considerable attention is now being paid to zinc deficiency as a crop-limiting factor in parts of the world besides Australia. Zinc sulphate additions have increased potato yields[32] and the same material has corrected deficiency disorders of fruit trees.[33] Two exceedingly useful books have been published in America during the year. One is a new edition of the National Fertilizer Association's 'Hunger Signs in Crops'; the other is 'Diagnostic Techniques for Soils and Crops' from the American Potash Institute.

References

1 Sherwin, K. A. and Steventon, J. W., *Chem. & Ind.*, 1949, **105** (also pre-print)
2 Procter, J. T., *Fertil. Soc. Proc.*, 1949, No. 7, 1
3 Sackett, W. J., *Ind. Eng. Chem.*, 1949, **41**, 1306
4 Atwell, J., ibid., 1318
5 Whitney, W. T. and Hollingsworth, C. A., ibid., 1325
6 Ettle, G. W., *Fert. Soc. Proc.*, 1949, No. 5, 47
7 Schulte, E. V., *Agric. Chem.*, 1948, **3**, 28
8 Report of Mineral Development Committee, 1949, pp. 44, 47 (H.M.S.O.)
9 Hull, S., *Chem. Engng*, 1949, **56**, 115
10 Davies, G. R. *et al.*, *Fertil. Soc. Proc.*, 1949, No. 5, 11, 63
11 Rader, L. F., *Amer. Fertil.*, 1948, **108**, No. 12, 7
12 Parker, F. W., *Agric. Chem.*, 1949, **4**, No. 3, 28

[13] *Fertil. J.*, 1949, **35**, 165
[14] 'Efficient Use of Fertilizers,' 1949, F.A.O. Agric. Study, No. 9, 173
[15] Crowther, E. M., *J. Roy. agric. Soc.*, 1948/1949, 71
[16] Idem, *Chem. & Ind.*, 1949, 808
[17] Hill, W. L. *et al.*, *Ind. Eng. Chem.*, 1949, **41**, 1328
[18] Report of Committee on Industrial Productivity, 1949, pp. 10, 19 (H.M.S.O.)
[19] Russell, E. J., *Brit. Ass.*, 1949
[20] Stewart, A. B., *Chem. & Ind.*, 1949, 271
[21] Cooke, G. W., *Fertil. Soc. Proc.*, 1949, No. 6, 1
[22] Idem, *World Crops*, 1949, **1**, 32
[23] Idem, *Chem. & Ind.*, 1949, 271
[24] Williams, E. G., *N.A.A.S. Quart. Rev.*, 1949, **1**, 147
[25] Hopkins, D. P., *World Crops*, 1949, **1**, 118
[26] Holmes, W., *Scott. Agric.*, 1949, **28**, 205
[27] Anon., *Fertil. J.*, 1949, **35**, 739
[28] *Soil Sci.*, 1949, **68**, 113 (12 papers)
[29] Bear, F. E., *Agric. Chem.*, 1949, **4**, 39
[30] Wallace, T., *J. roy. hort. Soc.*, 1948, **73**, 366
[31] Gilbert, F. C., *Agric. Chem.*, 1949, **4**, 24
[32] Terman, G. L. and Hawkins, A., *Amer. Fertil.*, 1948, 26
[33] Mulder, D., *C.R. Acad. agric. Fr.*, 1948, **34**, 177

CROPS (J. B. E. Patterson)

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Potatoes

ONE of the mainstays of this country's food production for the past ten years has been the potato crop; although the acreage to be grown next year under the Agricultural Expansion Programme is slightly less than in the peak year of 1945–6, it is unlikely that it will fall back to cultivation only in early districts or those specially suitable for heavy crop production. Many farmers have gained experience in the technique of husbandry and, as Cross[1] points out, 'we must see that all parts of the country carry a production quota compatible with the capacity of any particular soil to carry a profitable potato crop. Unless this is done there will be the tendency for the country's potato acreage to be concentrated once again into old intensive production areas where potato eelworm is rife.' His paper is one of a set of three forming a Symposium on the Potato Crop in which he deals with husbandry and cultural factors,[1] Crowther[2] with manuring and Samuel[3] with the control of potato diseases. Taken together, they form a valuable compact guide to potato growing in England to-day. Cross[1] emphasizes that soil preparation should begin as soon as one can get on to the land and that ploughing should be as deep as possible to 16 in. so that weed seeds are buried below the depth of ploughing likely to be used for subsequent crops in the rotation. A table shows the relation between crawler tractor sizes of a wide range of makes with various types of ploughs. All the processes of cultivations, ridging, planting, earthing-up, lifting, harvesting and storage are fully discussed. In a discussion of the best practice in potato planting Bohm[4] has concluded that the best yields per unit area are given by the earliest possible

planting and by spacing the set about 30 cm. apart, whereas Singh and Wakankar[5] found that the most economical method was to use the smallest seed at 9-in. spacing after comparing the effects of spacing at 6, 9 and 12 in. in rows 24 in. apart of seed sizes $\frac{1}{4}$–1 in., 1–1$\frac{1}{2}$ in., and 1$\frac{1}{2}$–2 in.

The effects of climatic factors such as latitude, altitude and the resulting types of season, temperature and length of day have been discussed for Tanganyika[6] and other places at low latitudes and high altitudes[7] where day-length is short. Hawkes[8] found that 'bolter' types of Gladstone and Sharpe's Express were taller, flowered more freely, matured earlier, and produced more stolons and a larger number of tubers than normal types under long-day conditions, whereas the differences between the types disappeared under short-day conditions. He suggests that mutation of unstable genes controlling response to day-length brings about change from normal to 'bolter' types. Further work on photoperiodism has been done by Edmundson.[9]

The course of growth of the potato plant is discussed by Balk[10] who shows that it is founded on the principle of competition for the available metabolites between the various plant organs, so that differences in growth form, maturity and yield of different varieties and strains under similar environmental conditions may be accounted for by division of these metabolites in various proportions between the organs at different growth stages. Other factors affecting yield and maturity are the size of leaves formed initially on the main stem, the length of time the size of haulm remains unchanged and the rate at which reserves of food materials in the foliage and roots are transferred to the tubers. Quantitative expression to the rate of absorption and translocation of mineral nutrients under conditions in Maine has been given by Hawkins[11] who found that 8·1% of total major nutrients were taken up and 3·2% of total growth were produced in the first 50 days of growth. In the next 30 days 71% of the major nutrients were taken up and 50% of total dry weight was formed. The greatest amount of dry matter was laid down about 10 days after the highest rate of nutrient absorbtion occurred between 30 and 40 days after emergence. The daily uptake of an acre of potatoes during the 10 days of greatest demand for nutrients was N 3·8, P_2O_5 0·6, K_2O 6·4, CaO 1·6, MgO 0·9 and S 0·3 lb. per day.

The manuring of potatoes had been investigated before the war and the general principles of sound practice were well established, but the Surveys of Fertilizer Practice carried out jointly by the Advisory Staff of the Ministry of Agriculture and the staff of Rothamsted Experimental Station showed how greatly practice varied from one country to another. Crowther and Yates[12] examined the results of a very large number of experiments with crops and suggested that for main-crop potatoes the most profitable dressing was N 0·91, P_2O_5 1·32 and K_2O 1·44 cwt. per acre without dung and N 0·87, P_2O_5 0·94 and K_2O 0·84 cwt. per acre with dung at 10 tons per acre. In his recent review of the manuring of potatoes, Crowther[2] suggests that the mean of these figures, giving a N : P_2O_5 : K_2O ratio of 1 : 1 : 1·5 is suitable for a wide range of soils, although local adjustments may be advisable such as an increase in the K_2O on light sands, in P_2O_5 on heavy loams and a reduction of N in wet regions. Dung is

more profitably employed on the potato crop than on any other and it, as well as fertilizers, should be placed in the bouts immediately before planting, thus giving the advantage of 'controlled placement.' The broadcasting of 7 cwt. per acre of fertilizer after ridging but before planting has been shown by Cooke[13] to be equal in effect to broadcasting of 10 cwt. on the flat before ridging and that placing the fertilizer in bands below or to the side of the sets is inferior to broadcasting. These recommendations are contrary to those given by Brown[14] who found that the most efficient method was placement in two bands. The explanation of this apparent disagreement lies, as emphasized by Crowther,[2] in the fact that British practice is to use whole sets planted on ridged land, whereas American practice is often concerned with cut sets planted mechanically on flat land.

The need for use of land uncultivated for many years during the war produced a number of instances of failure of potatoes from calcium deficiency as shown by poor growth with waxy distorted shoots and very small tubers. Davies, Fagan and John[15] have described the effects on acidic bracken land under a range of fertilizer treatments and show that with a proper supply of calcium and a reasonable balance between the other constituents crops of satisfactory quality can be grown. Manganese toxicity, as well as deficiencies of Mg, N, P, K and Ca, occurs on crops grown in reclaimed heathland at a p_H of 4·0.[16]

Rapid chemical tests for diagnosis of mineral deficiencies have been developed by Nicholas[17] who found good correlation between visual method, ash analysis and rapid tissue tests using sample of potato leaf-petiole midway between leaf attachment and the base of the lamina. Similar work has been described by Nylund.[18] Micro-nutrient studies have been made by Hawkins, Chucka and Brown[19] who found depression in yield on application to a soil at p_H 5·0 of 100 lb. per acre Cu, Zn or Ni sulphates while 50 lb. per acre of Cu, Fe or Zn sulphates had no effect. No consistent relation was found between boron content of different varieties grown at different locations by MacVicar *et al.*[20] who found the range of boron content in oven-dry material in μg. per g. was: leaf, 20·9–73·8, stem, 19·0–16·6, and tubers, 5·5–13·9. Plant, Hewitt and Nicholas[21] studied the effect of lime and fertilizers on a strongly acid soil by visual symptoms and chemical tests and found that Mg deficiency symptoms appeared if it was not supplied. Further work on Mg deficiency is described by Nicholas and Catlow.[22]

Correct fertilizer treatment has great effect on quality of potato tubers, which means to the consumer mostly resistance to blackening and the degree of mealiness on cooking. Pollard, Kieser and Crang[23,24] show that blackening on cooking depends partly on deficiency of K, but largely on site and variety. High N combined with low K tends to increase blackening. Red King and Kerr's Pink were found to be more resistant to blackening than Arran Banner, Majestic, King Edward, Gladstone and Dunbar Rover. Discoloration after cooking was related by Bandemer *et al.*[25] to moisture, ash, Mn, Fe and p_H, and is stated to vary with the increase of moisture and decrease of p_H. The latter statement is supported by Smith *et al.*,[26] who also show that blackening occurs most severely in tubers which mature at a low temperature. Wager[27] found

that the amount of blackening increases during storage at 8° C. and that much of the pigment develops in tubers stored at low temperatures immediately after lifting. Smith *et al.*[26] prevented all blackening by storage for 4 days at 37·8° C. That earliness in lifting reduces the tendency is agreed by Wager[27] and Smith and Nash.[28] The partial characterization of the compound responsible is reported by Isherwood,[29] who showed that tyrosinase was not implicated (as is supported by Nash[30]), and by Lewis and Doty[31] who extracted a colourless precursor of the pigment by extraction of fresh tubers with acidified alcohol. After removal of water and alcohol in presence of *iso*butyl alcohol the pigment is precipitated by ether and has been shown not to contain tyrosine or tryptophan.

Periodic shortages of seed potatoes caused either by disease in the preceding year's crop or by sudden increased demand have led to reconsideration of the usual methods of using whole sets, and the use of eye sets is described by Marritt[32] who recommends treatment of the whole tubers with fungicide (organic Hg preparations) before cutting, removing eye-sets not less than $\frac{7}{8}$ in. in depth and 0·5 oz. in weight, washing them in water, packing immediately in waterproof containers, and storing at 25° C. for 4–7 days and subsequently at 3·3° C. until sent away. Wakankar[33] recommends that pieces of about 1·5 oz. with up to 3 sprouts give better results, and Klitsch[34,35] supports his views with the modification that two pieces of about $\frac{3}{4}$ oz. each should be sown in pairs, coupled with the warnings that any piece having less than three eyes is likely to be uneconomic and that cut eye-sets are more susceptible to virus attack than whole seed. Treatment of cut sets with zinc oxide to prevent premature rotting and to encourage suberization is recommended by Bald.[36,37] Broadfoot[38] emphasizes the importance of adequate suberization to prevent *Penicillium* infection, especially as 5% aqueous boric acid is the only fungicide effective in the absence of a good surface layer of corky tissue.

Plant hormones have been used in late years for controlling the sprouting of potatoes while in store. Thomas and Riker[39] in comparing the effect of five different hormones found that methyl α-naphthylacetate (MANA) applied as a talc dust or spray was the most effective. Luckwill[40] supports this and finds that talc and shredded newspaper were the best carriers when the substance is used at the rate of 0·5–3·0 oz. per ton of tubers. In a later paper[41] he shows that the methyl ether (MNME) is equally effective and that treated potatoes remain firmer than untreated ones. Other substances besides hormones have been tried as sprout inhibitors, and Kardos and Blood[42] claim that carbon dioxide at concentrations between 10·5 and 11·8% by volume is as effective as a talc dust containing 0·4% MANA. 5% Tetrachlornitrobenzene dust has been used by Brown[43] for reducing winter sprouting of early potatoes. It was better than 20% pentachloronitrobenzene. Both compounds protected emerging shoots from *Rhizoctonia solani.*

Ethylene chlorohydrin has been used to produce the reverse effect in stimulating shoot growth. Porter and Simpson[44] use it for giving advance information on the virus content of seed stocks harvested four months previously, while Pujals *et al.*[45] treated seed potatoes previously sprayed

or dusted with MANA or ethyl 1-naphthylacetate and found that sprout emergence was slow and yield reduced.

2, 4-D according to Bradley and Ellis,[46] and Thompson and Shuel[47] gives control of broad-leaved weeds with no ill-effects on potato yield when applied at the rate of 1·2 lb. free acid or ⅞ lb. Na salt per acre. Its use, incorporated in regular sprays, is advocated.

Control of blight by destruction of the haulms is becoming more widely practised. Sulphuric acid is the most effective material but its corrosiveness makes it unpopular so that much work is being done to find more pleasant substitutes. Wilson *et al.*[48,49] find that 1 : 10 or 1 : 20 tar acid emulsion is 90% as effective as sulphuric acid and harmless to skin and clothing, 1·5% sodium chlorate is good and cheap but does not kill the stems; cyanamide, copper chloride and nitrate, DNOC, tar-oil winter wash, and copper sulphate–sodium chloride were only moderately effective. The authors emphasize the importance of killing off the haulm by actual wetting by the spray to destroy the fungus spores. Main and Grainger[50] also recommend 1·2% sodium chlorate in water at 100 gal. per acre. Trials in America described by Collbeck,[51] and McGoldrick and Smith[52] employed a number of proprietary materials as well as plant hormones, sodium nitrite and sodium arsenite. The last with fuel oil appeared to be the most destructive.

Root crops

Statistical examination of the results of long-term experiments on crops gives much information on the effect of fertilizer treatments and seasonal variation in weather conditions on yields. The results of the Barnfield experiments on mangolds carried out at Rothamsted between 1876 and 1940 have been discussed by Watson and Russell[53,54] who show that although if dung is given the effectiveness of extra potassium, sodium chloride and, sometimes, nitrogen is reduced, its use for this crop is justified. Inorganic potassium is not always needed, especially when sodium chloride is given. Joint use of dung and fertilizers slightly reduces the dry matter content of the plants. Rainfall in the two-monthly periods May–June, July–August and September–October does not correlate with seasonal variation in dry matter of leaves and roots, whereas the regression curve on time and accumulated rainfall fits the moisture content of the crop at intervals during the growing season very well.

Applications of nitrogen increase the nitrogen content of the leaves and the percentage in the residual dry matter of roots, and these show large seasonal variations, the values in roots depending on the yields and on the rainfall in the early part of the growing season. Potassium fertilizers tend to reverse the effects of nitrogen fertilizers. Applied nitrogen progressively reduces the percentage of sucrose in whole roots, but gives no consistent effect on reducing-sugar content.

Comparison of the percentage recovery of nitrogen applied in various forms showed that sulphate of ammonia gave low recovery, which was increased by farmyard manure; sodium nitrate gave 60% recovery.

The nitrogen and sugar content of sugar beet are affected by leaving the beet in the field after being topped before being picked up. Fife and

Price[55] found that soluble and noxious nitrogen increased for the first two days, while sucrose decreased at a steady rate of 4·8 lb. per ton fresh sugar beet roots per day exposure, and the loss of total sugar mostly through respiration was between 4% and 9% over a 5–8 day period.

Segmented seed has been used in several countries as a means of economizing seed, hastening germination and simplifying subsequent cultivation. Details of the methods used and the advantages in the U.S.A. and Holland have been described by Duborg[56] and van Scherpenberg[57]; Basséguy[58] discussed some of the difficulties of sowing and showed how coating the seed with talc or similar materials would largely overcome them. The coating process may be further developed by incorporating fertilizers, insecticides and growth hormones, and a 10–15% increase in yield has been claimed from the use of the two last. This contrasts with the experience of Stout and Tolman[59] who tried naphthylacetic acid and its amide, indolyl-acetic and -butyric acids, and laevulinic acid at 10–1000 p.p.m. in dusts and 2–85 p.p.m. in sprays without significant effect on seedling emergence, vegetative growth, sucrose content, purity or yield of roots. Heavy seeding rates, on the other hand, are advocated by Sayre and Vittum[60] as a means of offsetting the stimulating effect of application of NaCl at 500 lb. per acre. Such dressings may produce undesirably large roots and heavy seeding rates reduce this tendency by interplant competition.

The effects of climate on yield and growth conditions of sugar beet have been studied by Hallgren[61] and Lesch,[62] and the importance of good rainfall in May and June for spring grown roots is emphasized. Gypsum is recommended as a liming material for the crop by Ragaller,[63] and Schropp and Arenz[64] have found boron residues and sludges to be as effective as pure borax in the control of heart rot.

References

1 Cross, P. E., *J. roy. agric. Soc.*, 1948, **109**, 98
2 Crowther, E. M., ibid., 114
3 Samuel, G. G., ibid., 118
4 Bohm, F., *Dtsch. Landw., Berl.*, 1947, **1**, 53
5 Singh, B. N. and Wakankar, S. M., *J. Amer. Soc. Agron.*, 1943, **35**, 613
6 Glorer, J., *Emp. J. exp. Agric.*, 1947, **15**, 9
7 van der Plank, J. E., ibid., 1
8 Hawkes, J. G., ibid., 216
9 Edmundson, W. C., *Amer. Potato J.*, 1941, **18**, 100
10 Bald, J. G., *Emp. J. exp. Agric.*, 1946, **14**, 43
11 Hawkins, A., *J. Amer. Soc. Agron.*, 1946, **38**, 667
12 Crowther, E. M. and Yates, F., *Emp. J. exp. Agric.*, 1941, **9**, 77
13 Cooke, G. W., *J. Agric. Sci.*, 1949, **39**, 96
14 Brown, B. A., *Amer. Potato J.*, 1945, **22**, 33
15 Davies, R. O., Fagan, T. W. and John, J. L., *Empire J. exp. Agric.*, 1944, **12**, 54
16 Wallace, T., Davies, W. M., Nicholas, D. J. D. and Hewitt, E. J., *A.R. agric. hort. Res. Sta. Bristol*, 1946, 61
17 Nicholas, D. J. D., *J. hort. Sci.*, 1948, **24**, 72 and 106
18 Nylund, R. E., *Amer. Potato J.*, 1948, **25**, 216
19 Hawkins, A., Chucka, J. A. and Brown, B. E., ibid., 1941, **18**, 234
20 MacVicar, R., Tottingham, W. E. and Riemen, G. H., ibid., 249
21 Plant, W., Hewitt, E. J. and Nicholas, D. J. D., *A.R. agric. hort. Res. Sta. Bristol*, 1947, 97
22 Nicholas, D. J. D. and Catlow, E., ibid., 110

[23] Pollard, A., Kieser, M. E. and Crang, A., ibid., 1946, 158
[24] Idem, ibid., 1947, 233
[25] Bandemer, S. L., Schaible, P. J. and Wheeler, E. J., *Amer. Potato J.*, 1947, **24**, 1
[26] Smith, O., Nash, L. B. and Dittman, A. L., ibid., 1942, **19**, 229
[27] Wager, H. G., *J. Agric. Sci.*, 1947, **37**, 270
[28] Smith, O. and Nash, L. B., *J. Amer. Soc. Agron.*, 1942, **34**, 437
[29] Isherwood, F. A., D.S.I.R. Food Investigation Board Report, 1939, 87
[30] Nash, L. B., *Amer. Potato J.*, 1941, **18**, 91
[31] Lewis, W. R. and Doty, D. M., *J. Amer. chem. Soc.*, 1947, **69**, 521
[32] Marritt, J. W., *Sci. Agric.*, 1944, **24**, 526
[33] Wakankar, S. M., *J. Amer. Soc. Agron.*, 1944, **36**, 32
[34] Klitsch, C., *Dtsch. Landw. Berl.*, 1948, **2**, 29
[35] Idem, ibid., 53
[36] Bald, J. G., *J. Counc. Sci. ind. Res., Aust.*, 1947, **20**, 87
[37] Idem, ibid., 190
[38] Broadfoot, J., *Emp. J. exp. Agric.*, 1947, **15**, 227
[39] Thomas, J. E. and Riker, A. J., *Amer. Potato J.*, 1945, **22**, 104
[40] Luckwill, L. C., *A.R. agric. hort. Res. Sta. Bristol*, 1946, 79
[41] Idem, ibid., 1947, 137
[42] Kardos, L. T. and Blood, P. T., *Amer. Potato J.*, 1947, **24**, 39
[43] Brown, W., *Ann. appl. Biol.*, 1947, **34**, 422
[44] Porter, W. F. and Simpson, G. W., *Amer. Potato J.*, 1947, **24**, 9
[45] Pujals, E. A., Nylund, R. E. and Krantz, F. A., ibid., 47
[46] Bradley, R. H. and Ellis, N. K., ibid., 1948, **25**, 87
[47] Thompson, D. W. R. and Shuel, R. W., ibid., 163
[48] Wilson, A. R., Boyd, A. E. W., Mitchell, J. G. and Greaves, W. S., *Ann. appl. Biol.*, 1947, **34**, 1
[49] Wilson, A. R. and Boyd, A. E. W., *Agriculture*, 1947, **54**, 201
[50] Main, A. D. C. and Grainger, J., *Scot. J. Agric.*, 1947, **27**, 14
[51] Calbeck, L. C., *Amer. Potato J.*, 1948, **25**, 225
[52] McGoldrich, F. and Smith, O., *Proc. Amer. Soc. hort. Sci.*, 1948, **51**, 401
[53] Watson, D. J. and Russell, E. W., *Empire J. exp. Agric.*, 1945, **13**, 61
[54] Watson, D. J., ibid., 1946, **14**, 49
[55] Fife, J. M. and Price, C., *J. Amer. Soc. Agron.*, 1947, **39**, 327
[56] Dubourg, J., *Industr. agric. aliment.*, 1947, **64**, Nos. 1–3, 9
[57] van Scherpenberg, A. L., *Chem. Weekbl.*, 1948, **44**, 292
[58] Basséguy, L., *Industr. agric. aliment.*, 1947, **64**, 369
[59] Stout, M. and Tolman, B., *J. Amer. Soc. Agron.*, 1944, **36**, 141
[60] Sayre, C. B. and Vittum, M. T., *Proc. Amer. Soc. hort. Sci.*, 1948, **52**, 398
[61] Hallgren, G., *K. Landtbr. Akad. Ann., Högskol.*, 1947, **14**, 173
[62] Lesch, W., *Bodenk. Pfl. Ernähr.* 1948, **42**, 47
[63] Ragaller, F., ibid., 1947, **39**, 35
[64] Schropp, W. and Arenz, B., ibid., 1948, **42**, 124

HORTICULTURE (O. Owen)

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Growth-regulating substances

THERE appears to be no diminution of interest in this group of compounds. In his presidential address to the British Association Sir John Russell[1] stated that in this country about 50 compounds had been examined for activity. One manufacturer lists over 50 compounds which have been or are suspected of having growth-regulating properties. Although a number of the many papers which have appeared during the year appear

to repeat earlier work, there is ample justification for this as some of the results are apparently contradictory and local conditions often have an effect on experimental findings. A complication which is liable to be overlooked is that different varieties of the same subject may react differently to the same treatment. C. H. Dearborn, R. D. Sweet and J. R. Harris[2] find that 2 : 4-dichlorophenoxyacetic acid (2, 4-D) used at rates of 0·2, 0·4 and 0·6 lb. per acre to control weeds in sweet maize is liable to cause injury to the maize, the extent of the injury depending on varieties. N. K. Ellis and E. T. Bullard,[3] however, show that 0·7 lb. per acre of 2, 4-D controlled *Abutilon theoprasti* in sweet maize and 18 varieties of maize showed no difference in susceptibility to injury as estimated by yields. They also show that the sodium triethanolamine and alkanolamine salts and *iso*propyl and butyl esters were equally effective. A new aspect of the use of these compounds is indicated in a paper by D. L. F. Franklin[4] which describes attempts to induce hard-headed lettuce to bolt and seed. He finds that in the variety Great Lakes 96% of plants formed seed stalks when treated with the ammonium salt of 2, 4-D at a concentration of 20 p.p.m.

Several papers have dealt with the effects of growth-regulators on fruit in storage. F. Gerhardt and E. Smith[5] show that immersion of apricots, peaches, apples and pears in aqueous 2, 4-D at 100 p.p.m. or 1000 p.p.m. or aqueous sodium naphthylacetate at the same concentrations is without effect. Similarly R. E. Marshall, C. L. Hamner and J. C. Kremer[6] find that wrapping fruits in paper impregnated with methyl naphthylacetate at 1000 p.p.m. was without effect on ripening at 1° c. or at room temperature. In this country L. C. Luckwill[7] shows that dipping Allington Pippin and Edward VII apples in naphthyl- or naphthoxyacetic acids at 10 p.p.m. or 100 p.p.m. had no effect on storage life.

After-effects of treatment by growth-regulating substances is an ever-present possibility. In this connexion H. H. Moon, L. O. Reigembal and C. P. Harley[8] sprayed two varieties of apple trees with 2, 4-D at the high concentration of 8100 p.p.m. from the air in November. Leaves on these trees remained there during the winter although they were dead and even when blades had been broken off the petioles remained. In the spring foliation was delayed and new primary leaves were badly deformed and showed typical epinasty; two other varieties did not show these injurious effects. Fruit-fall in the following season was markedly delayed.

A boon to the many who find fig seeds irritating is foreshadowed in work carried out by J. C. Crane and R. Blondean.[9] They show that neither β-naphthoxyacetic acid nor 2,4-D produce parthenocarpy in Calimyra figs when injected into the immature fruit or when used as sprays, but spraying with oil emulsions containing 1500 to 2760 p.p.m. 3-indolylacetic acid produced a satisfactory crop of seedless fruit.

The effects which may be produced on the economy of the plant have received attention. A. Rhodes, W. G. Templeman and N. W. Thurston[10] find that 4-chloro-2-methylphenoxyacetic acid (MCPA), when applied to the roots of rape, markedly depressed the potassium content of the tops, but it had no appreciable effect when applied to maize, chamomile or oats. When added to culture solution applied to tomatoes MCPA caused an appreciable reduction in the potassium content of the tops and reduced

that of the roots. This effect appears to be specific for potassium and does not apply to phosphorus, calcium, magnesium, sodium, manganese, copper, iron and total nitrogen. A quite different aspect is dealt with by H. M. Sell, R. W. Luecke, B. M. Taylor and C. L. Hamner.[11] They show that red-kidney-bean plants treated with 2,4-D accumulate protein and amino-acids to a greater extent than untreated plants; the suggestion is made that there is an alteration in the character of the protein. Differences are also caused in carbohydrate distribution and this may involve conversion of carbohydrates into lipin material. S. G. Wildman[12] suggests that tryptophan is one of the principal precursors of auxin in plant tissue. F. Nysterakis[13] having shown that the aphis *Anuraphis helichrysi* secretes indolylacetic acid concludes that inhibition of growth of stems of plum trees whose leaves are attacked by the aphis is due to injection of the auxin.

Finally a contribution which may throw light on the role of some organic nitrogenous materials in soil is made by J. H. Hamence.[14] He shows that 96% of β-indolylacetic acid added to soil is destroyed within 24 hours. Heavy dressings of dried blood or fish meal cause a transitory high level of soil auxins but values soon fall to normal. A mechanism controlling the 'auxin balance' in soil is suggested and this tends to keep the concentration within limits, the upper of which is harmless to plant growth.

Mineral nutrition of plants

A feature which is noticeable in current researches on the correction of mineral deficiency is the interest in changes in the composition of the plant and in its internal economy generally. With molybdenum, for example, there appears to be general agreement that one of its functions is to catalyse the reduction of nitrates in the tissue; in its absence nitrate tends to accumulate. For instance, E. J. Hewitt and E. W. Jones[15] conclude that in tomato, mustard and cauliflower, deficiency of molybdenum is associated with accumulation of nitrate in the petioles and increased osmotic pressure in the stomatal guard-cells. Working on cauliflower, which is one of the classical subjects for molybdenum-deficiency studies, R. D. Wilson and E. J. Waring[16] show that an intervenal chlorosis is corrected within seven days after treatment with molybdenum. Within two-and-a-half to five days after treatment no nitrate was found in the young leaves although it was present in older leaves.

That manganese may have similar effects is suggested by L. H. Jones, W. B. Shepardson and C. A. Peters[17] who advance the view that it is a catalyst without which reduction of nitrate to amino compounds either does not occur or only takes place at a much slower rate.

Possible mutual effects of manganese and molybdenum together are the subject of a preliminary note by E. J. Hewitt, E. W. Jones and A. H. Williams.[18] Cauliflower plants of the variety Majestic were grown in sand culture at three different levels of supply of each element, concentrations covering the range from deficiency to toxicity levels. In general a reduction in the molybdenum level was accompanied by a reduction in amino-acid concentration in the tissue but a reduction in the manganese level was associated with an increase in amino-acid concentration. The effect of change in molybdenum was most pronounced at manganese

deficiency levels but the effect due to change in manganese was more marked at a high molybdenum level. The changes were shown for arginine, alanine, proline, asparagine, glutamine, aspartic and glutamic acids. Not all these compounds showed variation over the ranges of both the manganese and molybdenum concentrations used.

On the practical side J. H. Quastel, E. J. Hewitt and D. J. D. Nicholas[19] showed that addition of sodium or calcium thiosulphate to a manganese-deficient soil caused an increase in manganese content of oats and reduced the symptoms of grey speck. In the field placement of thiosulphate was more effective than broadcasting in improving growth and reducing signs of manganese deficiency in beets without reducing the soil reaction. Placement of sulphur caused similar effects and lowered the soil p_H. It is considered that the action of sulphur may be due to slow formation of thiosulphate and acid formation. W. O. Robinson and G. Edgington[20] show that over-liming may increase the uptake of molybdenum in pastures to make the herbage toxic to animals. Vegetation whose toxicity has been attributed to a high selenium content was found to be rich in molybdenum also and it is suggested that the excessive molybdenum may contribute to the toxicity. H. D. Morris[21] working with legumes in culture found that increasing the calcium in the solution from 12 to 300 p.p.m. or of phosphorus from 2 to 20 p.p.m. were without effect on signs of manganese toxicity. E. J. Hewitt[22] on the other hand shows that signs of manganese toxicity in other subjects can be reduced or eliminated by increasing the calcium content of the nutrient solution. With cereals, however, he finds[23] that to increase the calcium in the nutrient solution is not so effective in counteracting the symptoms of aluminium toxicity as is the additiin of 0·1% of calcium carbonate to the sand.

W. L. Powers and T. S. Pang[24] report that on zinc-deficient soils 40–80 lb./acre of zinc sulphate corrects the condition. This treatment resulted in accelerated germination, pollination and maturation of plants while it improved root development and prevented 'little leaf' in stone fruit. Correction of 'little leaf' in grape vines by zinc sulphate is also reported by H. H. Kemp.[25]

B. F. G. Levy[26] describes a pitting in apples which is similar to but not identical with bitter pit. The disorder is alleviated by injection of 0·1% boric acid with an N–P–K mixture into the trees. This pitting is possibly related to 'corkiness.' In tomatoes E. G. Brennan and J. W. Shine[27] show that in normal leaves the calcium/boron ratio varies from 201 to 593; in leaves suffering from boron deficiency from 1000 to 2380 and in leaves suffering from boron toxicity from 30 to 114. At any boron level the calcium/boron ratio in tissue is markedly increased by increase in the calcium level in the substrate. Working with spinach plants in nutrient solutions P. N. Scripture and J. S. McHargue[28] conclude that 1 p.p.m. of boron is optimum for maximum yields but that increasing boron from 0·25 to 5 p.p.m. is accompanied by an increasing rate of protein synthesis in the tissue. C. H. Dearborn[29] shows that in both roots and heads of boron-deficient cauliflowers reducing-sugars were much greater than in the same parts of normal plants. W. O. Roberts[30] increased the yield of oats in a phosphorus-deficient soil from 17 to 25 cwt./acre by soaking the seeds in potassium phosphate. Oats soaked in 0·25 M-manganese

sulphate and planted in a manganese-deficient soil showed no deficiency symptoms in the early stages of growth. The same author describes[31] two novel modifications of the well known Roach injection method. One consists of drawing through the petiole a thread impregnated with the test solution. The other consists of applying a cotton wool pad impregnated with test solution to the wound caused by removing a leaf at the base of the petiole.

Vitamins in plants

F. G. Gustafson[32] finds that aneurin and riboflavin tend to be concentrated in leaves and stems, and older leaves are much richer in both vitamins than are ripe fruits. In a later paper[33] the same author shows that in the tomato, bean, pea and New Zealand spinach the concentration of aneurin is greater in plants exposed to high light intensity than in those grown in low intensity or in darkness. The effect of light is similar for riboflavin but is not so pronounced. In the case of cucurbits K. S. Wilson[34] shows that vitamin concentration decreases progressively with development after the early stages. In the fruits the niacin concentration was higher than that of aneurin or riboflavin, the respective concentrations being more related to physiological age than to fruit size. Aneurin concentration is related to seed development so that although vitamin concentration generally is similar in diploids and tetraploids there is a higher concentration of aneurin in the placental region of diploids on account of the larger number of seeds produced. F. J. H. Le Riche[35] has studied the mechanism of ascorbic acid synthesis in the guava. Glucose is absent but fructose persists and this latter corresponds to the ascorbic acid. On the assumption that sucrose is the sugar of translocation the following scheme is suggested to account for ascorbic acid formation : D-glucose → D-sorbital → L-sorbose → 2-keto-L-gulonic acid → L-ascorbic acid.

F. Wokes and R. Melville[36] have examined different tissues collected from the walnut during three seasons. They show that remarkably high concentrations of vitamin *C* occur in the endocarp and this may be used in lignification. Physiological conditions militate against translocation from the leaf to the nut. In the tomato F. Wokes, J. R. Barr, L. Brunskill and A. C. Shaw[37] conclude that calcium is the only constituent of fertilizers which has a significant effect on vitamin *C* production and that climatic conditions constitute the overriding factor. Four years' study of tomatoes under glass and out of doors lead A. Pollard, M. E. Keiser and J. D. Brian[38] to conclude that cropping capacity may well outweigh the actual ascorbic acid concentration in fruit if the total production of the vitamin per unit area is taken as the basis of comparison. Despite variation in the production in the same variety in different years they consider that varietal differences are established. M. B. Crane and S. S. Zilva,[39] on the other hand, as the result of extensive work conclude that there is no significant difference in varieties but they did not relate vitamin production to unit area. Ignoring the temperature differences involved they find that light of shorter wavelength favours ascorbic acid production in the tomato plant. This explains the differences in ascorbic acid

concentration in outdoor fruit and that grown under glass. It is assumed that glass filters off light of relatively low wavelength. They were unable to associate hours of sunshine with ascorbic acid production and this is attributed to the transparency of the atmosphere in the district where the plants were grown. The appearance of lycopin on ripening seems to play no part in ascorbic acid formation. Provided that they are exposed to the same illumination the concentration is higher in red than in green fruits but if green fruits be picked when they are fully grown they may be ripened artificially without loss of the vitamin.

References

[1] *Nature*, 1949, **164**, 385
[2] *Proc. Amer. Soc. Hort., Sci.*, 1948, **51**, 536
[3] Ibid., 506
[4] Ibid., 453
[5] Ibid., **52**, 159
[6] Ibid., **51**, 95
[7] *A. R. agric. hort. Res. Sta., Bristol*, 1947, 142
[8] *Proc. Amer. Soc. hort. Sci.*, 1948, **51**, 81
[9] *Plant Physiol.*, 1949, **24**, 44
[10] IInd Int. Congr. Crop Protect. Lond., 1949
[11] *Plant Physiol.*, 1949, **24**, 295
[12] Ibid., 84
[13] *C. R. Acad. Sci., Paris*, 1948, **226**, 746
[14] *J. Soc. chem. Ind.*, 1948, **67**, 277
[15] *J. Pomology*, 1947, **23**, 254
[16] *J. Aust. Inst. agric. Sci.*, 1948, **14**, 141
[17] *Plant Physiol.*, 1949, **24**, 300
[18] *Nature*, 1949, **163**, 681
[19] *J. agric. Sci.*, 1948, **38**, 315
[20] *Soil Sci.*, 1948, **66**, 197
[21] *Iowa St. Coll. J. Sci.*, 1948, **23**, 55
[22] *A. R. agric. hort. Res. Sta., Bristol.*, 1946 50
[23] Ibid., 1947, 82
[24] *Soil Sci.*, 1947, **64**, 29
[25] *J. Agric. South Australia*, 1946, **50**, 3
[26] *A.R.E. Malling Res. Sta.*, 1946, 95
[27] *Soil Sci.*, 1948, **66**, 65
[28] *J. Amer. Soc. Agron.*, 1944, **36**, 865
[29] *Cornell agric. exp. Sta.*, 1942, Bull. 778
[30] *J. agric. Sci.*, 1948, **38**, 458
[31] *J. Pomology*, 1946, **22**, 184
[32] *Plant Physiol.*, 1947, **22**, 620
[33] Ibid., 1948, **23**, 373
[34] *Amer. J. Bot.*, 1948, **34**, 469
[35] *J. S. Afr. chem. Inst.*, 1948, **1**, 35
[36] *Biochem. J.*, 1948, **43**, 585
[37] *J. Soc. chem. Ind.*, 1948, **67**, 262
[38] Ibid., 281
[39] *J. hort Sci.*, 1949, **25**, 36

ANIMAL NUTRITION (W. Godden)

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VARIOUS aspects of nutrition in relation to wool production have been studied by Marston[1] by feeding sheep at four different levels of nutrition, the highest being 400–600% above the lowest, and following the rate of wool growth, measuring the length and mean diameter of the fibres and determining the energy and nitrogen balances. Equilibrium between level of intake of a particular ration and rate of wool production becomes established only after a lapse of three months or more after relatively large changes in intake have been imposed. From calculations based on the amino-acid constitution of the proteins in the ration and of the main products (wool and flesh) it was concluded that the cystine and methionine contents of the food protein would limit to 27% the efficiency of its conversion into wool. Under the experimental conditions the efficiency of the utilization of the *S*-amino-acids for wool production was 47% with the best wool producer when it was in strongly positive energy balance and only 14% for the poorest producer when close to energy equilibrium.

The copper content of the ration or the pasture is an important factor in wool production.[2] Sheep pastured on an area where the copper content of the dry matter of the herbage was less than 3 p.p.m. showed symptoms of copper deficiency. There was a fall in the level of copper in the systemic blood and, when the level was below 0·4 mg. per l., the capacity to impart crimp to the wool fibres decreased and failed completely at a blood-copper level below 0·2 mg. per l. In groups of sheep receiving from 0 to 20 mg. copper daily the increments of increase in wool production over that of controls were related to the level of copper supplementation by a curve of diminishing returns. Supplements of 10 mg. or more of copper daily were adequate to maintain normal blood-copper levels and the capacity to impart crimp to the wool. An anonymous report[3] considers that copper deficiency in sheep delays the oxidative closure of –SH of prekeratin to –S–S– of keratin and the wool fibre extrudes from the follicle in a semi-plastic state to oxidize slowly in the air ; straight lustrous wool, which is a sensitive indicator of copper deficiency, is formed. The wool of black sheep becomes progressively less pigmented as the copper status is lowered. Adequate dosing with copper restores both crimp and colour to the new wool. Palm[4] considers that copper sulphate applied at an average of 7 lb. per acre to ironstone or sandy soils deficient in copper is sufficient to prevent 'steely' wool on sheep grazing on the pasture. Work by Lee and Moule[5] supports these findings. Bennetts *et al.*[6] found that cows and calves grazing on areas similar to the above also developed symptoms of copper deficiency, the principal pathological finding being a progressive myocardial atrophy.

Coastal disease in S. Australia[7] is due to a combined deficiency of copper and cobalt and the deficiency can be corrected by the administration of 2 mg. copper and 2 mg. cobalt thrice weekly. If only copper is given the animals show symptoms of cobalt deficiency and individuals die

within 1 year. Sheep receiving cobalt and no copper developed a hypochromic anæmia. Cobalt deficiency occurs also in New Zealand and McNaught[8] has studied the cobalt, copper and iron contents of the livers of healthy and bush-sick cattle and sheep, and has suggested diagnostic levels.

The use of monozygous twin calves has come into prominence for the study of certain problems in cattle feeding. Bonnier *et al.*,[9] from a series of long-term feeding and lactation experiments with numerous sets of twins in which one of each set received a normal ration and the other quantitatively less, showed that heredity plays a prominent part in the expression of practically all types of characters and usually outweighs the effects of fairly wide differences in nutritional levels. There is a ceiling beyond which it is not possible by feeding to push either weight, body size, milk yield or milk quality. Cows with high-yielding capacity were not more adversely affected by underfeeding than those with lower capacity, though the latter were adversely affected by overfeeding probably through metabolic disturbances. When excessive amounts of calcium and phosphorus were given for 45 days before the expected calving date to one of each set of monozygous twin heifers, otherwise identically fed, there was a slight decrease in total milk yield in a high-producing genotype and a slight increase in a low-producing genotype. In one set of monozygous twin heifers one of the animals calved prematurely and this resulted in an incompletely developed udder, which ceased to develop after calving and resulted in a lower total yield of milk and of the milk constituents although the actual percentages of fat, protein and lactose in the milk were higher.

The effect of the level of wintering steer calves on their subsequent summer gains has been examined by Darlow *et al.*[10] who found that steers which gained most during the winter gained the least on grass and that the most economical method of producing yearling steers is to winter at a low level with cured grasses as roughage and cottonseed meal and to provide ample herbage during the summer. Connell *et al.*[11] report the same type of result even when the animals were fattened after summer pasture and consider that protein supplementation during the winter would only pay if the steers were sold at the end of the winter period. For pigs on pasture it was found by Gobble *et al.*[12] as a result of four years' trials that (*a*) ladino clover pasture gave slightly faster and more economical gains than those on orchard grass (*b*) for pigs on ladino clover grass maize was not an adequate supplement for maximum growth but that a protein supplement containing 12% of protein was adequate, and (*c*) for pigs on these pastures soya-bean oil meal was a better supplement than tankage.

Burroughs and co-workers[13,14] have studied the influence of the protein level in the ration on the digestion of roughage, in the form of maize cobs or hay, by cattle. From a series of trials it is concluded that the protein requirement by the ruminant for efficient roughage digestion is low when the roughage is given in the absence of starch but that, when starch forms a part of the ration, the protein requirement is materially increased; why starch should cause this rise in protein requirement is not known. Watson *et al.*[15] on the other hand, found that the digestibility

of a ration of timothy hay–barley–soya-bean oil meal was not affected by varying the nutritive ratio within the range 1 : 2–9.

Bartlett and Blaxter[16] have again examined the value of urea as a partial substitute for protein in rations for dairy cows by a cooperative experiment on 12 farms using 274 dairy cows. They report that the addition of urea to a protein-deficient ration did not increase milk yield, although the addition of groundnut cake did give a significant increase. With a normal protein ration the addition of more than 3 oz. of urea daily tended to depress the milk yield, the effect being more marked with the higher-yielding cows. Sure[17] found little difference between dried food yeast, soya-bean flour, non-fat milk solids, or dried sweet cream buttermilk as supplements to the proteins of milled white maize meal but that cultured and brewer's yeasts were superior to soya-bean flour or groundnut flour as supplements for milled enriched wheat flour. The increase in the biological value of the protein of milled enriched wheat flour by the addition of dried food yeast was due to the lysine and possibly other dietary essentials in the yeast. To white maize meal its supplementary value is ascribed to lysine, tryptophan and other essentials.

Wound healing in rats was found by Kobak *et al.*[18] to be delayed by a low-protein diet up to the fifth day after which the tensile strength of the wounds rose in a fashion parallel to that in rats on adequate protein diet. This prolonged 'lag' in the onset of healing and delayed completion can be to a large extent overcome according to Localio *et al.*[19] by the administration of DL-methionine to the diet of the protein-depleted rats. It is suggested that a deficiency of thiol enzymes may be one of the reasons for the delayed healing in protein deficiency.

The nutritive value of acid hydrolysates of protein has been examined by various workers. Frost and Sandy[20] describe a relatively rapid method for the assay of such liquid hydrolysates and conclude that the S-containing amino-acids in partial acid hydrolysates of casein are not completely utilized when administered orally to rats. Wissler *et al.*[21] have carried out biological assays on 25 commercial brands of hydrolysates and found great variations in the capacity of the hydrolysates to induce tissue synthesis in the protein depleted rat. Hydrolysates prepared from high quality animal proteins produced the greatest gains in experimental animals. Hanson and Schultze[22] concluded that neutralized hydrolysates of animal or vegetable protein were of value to man only as flavourings.

Woodman and Evans[23] have further investigated the minimum level of protein intake by pigs consistent with maximum rate of growth. They report that pigs on a low protein diet containing 7% of white fish meal up to a live-weight of 90 lb. and thereafter no protein-rich supplement showed live-weight increase and efficiency of food conversion equal to those of pigs receiving a standard protein diet containing 10% of fish meal up to 150 lb. live-weight and afterwards 5% of extracted decorticated groundnut cake instead of fish meal to slaughter weight. Crampton[24] found no beneficial effect on carcase quality by replacement of up to 20% of the protein in the form of oilmeal or oilmeal and wheat germ in a fattening ration for pigs by animal protein in the form of tankage. Braude, Henry and Kon[25] have carried out further studies of the rachitogenic

effect of dried yeast in pig diets. The results throw no further light on the nature of the substance in yeasts which causes rickets in pigs save to show that it is heat-stable and persists in autoclaved yeast. Its effect is not to inhibit the intestinal break-down of phytic acid.

Bailey *et al.*[26] compared the relative effects of 25, 50, 100 or 150 mg. L-thyroxine with that of 15 g. iodocasein all given orally daily to lactating cows. The respective increases in milk yield after 3 weeks were 1·6, 3·6, 5·9, 6·3 and 4·3 lb. per cow per day. On this basis 15 g. of iodocasein was only equivalent to 60 to 78 mg. L-thyroxine. Since iodocasein is believed to contain about 3% of thyroxine it was concluded that either the published estimates of the thyroxine content of iodocasein are wrong or that the efficiency of the oral utilization of the thyroxine in iodocasein is much lower than that of the pure hormone. Thomas *et al.*[27] fed thyroprotein for an average of 301 days to heifers during their first lactation at a rate of 0·6–1·5 g. per 100 lb. live weight. All the cows responded with an increase in milk production (fat corrected) but to a varying degree. When allowance was made for the nutrients needed for weight gains it was calculated that the control and treated cows consumed 60 and 65 lb. of total digestible nutrients respectively to produce 100 lb. of 4% milk. It was concluded that thyroprotein, at the rates given, did not significantly change the gross efficiency of milk production. Dryendahl[28] fed iodinated casein for long periods to cattle, swine and rats. Polled Swedish cattle of both sexes received the iodinated casein in some cases from birth and their progress was compared with similarly treated animals receiving no iodinated casein. The treated animals showed poorer digestive capacity than the controls and exhibited stiffness in the leg bones with noticeable swelling of the pastern joints. *X*-ray photographs of the lower tibia, the hock joint and the phalangeal joints of the forelegs showed that the porosity of the bone was much greater in treated animals than in controls of the same age. Similar experiments with pigs receiving 0·1 g. per 30 kg. and 1 g. per 100 kg. body weight respectively from weaning to 120 kg. live weight showed at slaughter results similar to those with cattle. The effect on the bone system was even more pronounced in the group receiving the higher dose and some animals had lost the use of their hind limbs. It was estimated that the control pigs required only 3·65 Scandinavian feed units per kg. increase in live weight whereas those on the low and high doses of iodinated casein required 4·20 and 5·0 units respectively.

The vitamin requirements of pigs have attracted attention during the period under review. Swank and Adams[29] have found that young pigs, fed on a synthetic diet deficient in pyridoxine, showed irreversible ataxia, weakness and convulsions shortly before death. On a diet deficient in pantothenic acid they developed diarrhoea, tongue lesions, ataxia and a high-stepping gait. The histological findings are reported. Deficiency of vitamin B_1, as well as of these two substances, can individually impair the metabolism of sensory neurones, but whilst the disabilities due to lack of vitamin B_1 are reversible, those due to deficiency of the others are not. Cartwright *et al.*[30] showed that weanling pigs, fed on a low protein diet deficient in nicotinic acid developed a normocytic anaemia. The anaemia responded to administration of a high protein diet or of nicotinic

acid. They conclude that nicotinic acid is essential for normal erythropoiesis when pigs receive diets low in protein. Luecke *et al.*[31] using a low-protein maize diet, containing 11·2 mg. nicotinic acid per lb., report that supplementation with 1 g. daily of DL-tryptophan prevented the appearance of symptoms of nicotinic acid deficiency and gave excellent growth and food utilization. Supplementation of the same ration with nicotinic acid (30 mg. daily) increased the utilization of its trypotophan. On a maize ration containing 25% casein and only 8·1 mg. nicotinic acid per lb. no symptoms of nicotinic acid deficiency were observed and the pigs grew rapidly and required only 2 lb. of feed to produce 1 lb. of body weight. Powick *et al.*[32] record similar experiments and consider that nicotinic acid was not completely effective as a substitute for tryptophan but that the latter was a satisfactory substitute for the former. Heifer calves on a ration of mixed hay, silage and grain mixture responded to the supplementation of the diet with 40,000 or 114,000 U.S.P. units of vitamin *A* daily by a highly significant increase in the rate of live weight gain (Ross and Knodt[33]). From Columbia, Alvarez[34] points out that keratitis, which is common among cattle during the dry season in some hot regions, was cured in 14 days by treatment with vitamin *A* injections. Warner and Sutton,[35] by using photolysed milk, in which 96% of the riboflavin had been destroyed, for feeding new-born calves estimated the minimum daily requirements of very young calves to be less than 75 μg./kg. body weight daily and considered that riboflavin deficiency was not likely to occur under normal conditions during the milk feeding period.

References

1 Marston, H. R., *Austral. J. sci. Res.*, 1948 [B], **1**, 362
2 Marston, H. R. and Lee, H. J., ibid., 376
3 21st A.R. Coun. sci. indust. Res. Austral., 1946–7, 36, 37
4 Palm, M. A., *J. Agric. South Australia*, 1946, **49**, 587
5 Lee, H. J. and Moule, G. R., *Austral. vet. J.*, 1947, **23**, 303
6 Bennetts, H. W. *et al.*, ibid., 1948, **24**, 237
7 Marston, H. R. *et al.*, *J. agric. Sci.*, 1948, **38**, 216, 222
8 McNaught, K. J., *N.Z. J. Sci. Tech.*, 1948, **30A**, 26
9 Bonnier, G. *et al.*, *Acta Agric. suecana*, 1948, **3**, 1, 59, 71
10 Darlow, A. E. *et al.*, *J. Anim. Sci.*, 1948, **7**, 536
11 Connell, W. E. *et al.*, ibid., 430
12 Gobble, J. L. *et al.*, ibid., 537
13 Burroughs, W. and Gerlaugh, P., ibid., 1949, **8**, 3
14 Burroughs, W. *et al.*, ibid., 9, 271
15 Watson, C. J. *et al.*, *Sci. Agric.*, 1947, **27**, 600
16 Bartlett, S. and Blaxter, K. L., *J. agric. Sci.*, 1947, **37**, 32
17 Sure, B., *J. Nutrit.*, 1948, **36**, 65
18 Kobak, M. W. *et al.*, *Surg. Gynec. Obstet.*, 1947, **85**, 751
19 Localio, S. A., ibid., 1948, **86**, 582
20 Frost, D. V. and Sandy, H. R., *J. biol. Chem.*, 1948, **175**, 635
21 Wissler, R. W. *et al.*, *J. Amer. diet. Ass.*, 1947, **23**, 841
22 Hanson, H. and Schultze, W., *Pharmazie*, 1948, **3**, 340
23 Woodman, H. E. and Evans, R. E., *J. agric. Sci.*, 1948, **38**, 354
24 Crampton, E. W., *Sci. Agric.*, 1946, **26**, 545
25 Braude, R. *et al.*, *Brit. J. Nutrit.*, 1948, **2**, 66
26 Bailey, G. L. *et al.*, *Nature*, 1949, **163**, 800
27 Thomas, J. W. *et al.*, *J. Dairy Sci.*, 1949, **32**, 278
28 Dryendahl, S., Thesis, Univ. Stockholm, 1949
29 Swank, R. L. and Adams, R. D., *J. Neuropath. exp. Neurol.*, 1948, **7**, 274

[30] Cartwright, G. E. et al., *Arch. Biochem.*, 1948, **19**, 109
[31] Luecke, R. W. et al., *J. Nutrit.*, 1948, **36**, 417
[32] Powick, W. C. et al., *J. Anim. Sci.*, 1948, **7**, 228
[33] Ross, R. H. and Knodt, C. B., *J. Dairy Sci.*, 1948, **31**, 1062
[34] Alvarez, J. G., *Amer. vet. med. Ass.*, 1947, **111**, 216
[35] Warner, R. G. and Sutton, T. S., *J. Dairy Sci.*, 1948, **31**, 976

VETERINARY MEDICINES (A. N. Worden)

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Sulphonamides

OBSERVATIONS upon the control of caecal coccidiosis in poultry have been extended. Prompt treatment of the condition in fowl chicks was found to be effective when either 0·2% of sodium sulphamerazine or sulphamethazine in the drinking water, or 0·5% of sulphamerazine, 0·4% sulphamethazine or 1·0% sulphaquanidine in the mash was given for two days, starting 72 hours after infection or upon the first appearance of symptoms.[1] There was not any retardation of growth or other harmful effect when the recommended amounts and schedules were employed. The unintentional substitution of a 1·0% for a 0·2% solution of sulphamethazine in the drinking water did not lead to any toxic effects.[2] The addition of 1·0% but not of 0·5% of phthalylsulphathiazole to the feed was successful.[3] Coccidiosis in turkeys was successfully controlled with sulphaquinoxaline given in the feed at the rate of 1 oz. to 200 lb. of mash (0·031%), the medicated feed being given for two days initially and thereafter being substituted for the regular mash every fourth day. There was a mortality rate of only 2%, compared with 38% in the untreated control group, while subsequent rate of gain was superior and culling losses were lower. In another flock similar treatments involving 0·031% sulphaquinoxaline, or 1·0% of sulphaquanidine or 0·5% of sulphamerazine were all successful.[4] Experimental and field outbreaks of fowl cholera (*Pasteurella septica*) in fowls[5] and turkeys[6] were successfully controlled with sulphamethazine and sulphamerazine. In the field outbreak in turkeys a blood concentration of about 14 mg. per 100 ml. was attained when 0·5% of sulphamerazine was incorporated in the mash for five days. The diseases in turkeys recurred on cessation of treatment but was controlled by reintroduction of the medicated mash. Sulphamethazine and sulphaquinoxaline were ineffective in outbreaks of ulcerative uteritis in quail,[7] but large outbreaks of cholera and of salmonellosis in ducks were successfully treated with sulphamethazine.[8]

Further reports were made of the value of sulphonamides in controlling 'foul of the foot' in cattle.[9–12] It is suggested that a dose of 60 g. is suitable for the average adult bovine.[9] Acute cases were found to respond much more readily than chronic.[10] Cases of apparently typical 'foul of the foot' in two calves, aged 19 and 34 days respectively, responded to sulphapyridine.[11] The intravenous injection of sulphathiazole produced good results also in the treatment of 'thrush' in horses.[12] 'Joint-ill' in foals

was stated to respond in 7 out of 9 cases to sulphamethazine administered subcutaneously.[13] The permeability of the lactating mammary gland to sulphonamides was studied : of seven compounds tested, only sulphamilamide and sulphapyridine appeared in the milk in concentrations approaching those attained in the blood.[14] The results of sulphamethazine in the treatment of acute and chronic bovine mastitis were favourably reported.[15] In cases of enterotoxaemia (*Clostridium welchii* type D) in goats the combination of 3 to 4 doses of sulphamezathine with 50 ml. of serum gave better results than serum alone.[16] A high percentage of cures was claimed (1 grain per lb. body-weight) following the intraperitoneal injection of sulphamethazine in cases of pasteurellosis and of 'bloody dysentery' in swine.[17]

p-*Aminobenzoic acid*

The growth of *Brucella abortus*, *B. melitensis* and *B. suis* was inhibited when 2 mg. per ml. of *p*-aminobenzoic acid was added to each ml. of (tryptose agar) culture medium. Experimental *B. abortus* infections in guinea-pigs were successfully treated, there being 100% 'sterilization' when the drug was administered 3 days after inoculation of the organisms, but clearance in 80% of cases when treatment was delayed for 14 days. The blood levels attained ranged from 15 to 45 mg. per 100 ml. In a few instances during early experiments there were deaths from shock following subcutaneous injection of the drug, but in general the treated animals showed rapid gains in weight as treatment progressed.[18]

Penicillin

There have been many further reports upon the penicillin treatment of bovine mastitis. Suspensions of penicillin in oil produced levels in the udder equal to those produced by infusions of similar doses in aqueous solution and produced very little disturbance to the udder tissue. The use of a separate tube for each treatment was strongly advocated to eliminate the risk of cross infection from a non-sterile infusion apparatus. Calcium penicillin (725 units per mg.) and crystalline penicillin G (1550 units per mg.) in similar doses produced similar levels in the milk. The addition of up to 6% of beeswax to penicillin suspensions did not appear to prolong penicillin levels in milk to any appreciable extent. Slender bougies, each containing 25,000 units of penicillin in a water-soluble base, caused little or no disturbance to secreting tissue and gave curative results comparable with those from similar doses in aqueous solution.[19] Procaine penicillin G became widely used for veterinary practice and in suitable formulations gave high and more persistant concentrations of penicillin in the udder.[19,20] It was suggested by one worker that with either calcium penicillin or with suitable preparations of procaine, penicillin injection once every three days might be adequate.[21] Good results were claimed from combined treatment with penicillin and bacitracin.[22] The post-treatment occurrence of streptococcal infection in the bovine udder may be very high,[23] and from controlled observations it would appear as if herd hygiene were an essential adjunct to penicillin therapy.[24]

In the treatment of clinical staphylococcal infections of the bovine udder penicillin alone and sulphone alone were disappointing, but a mixture of the two gave rather more promising results.[19] A further report appeared on the value of penicillin in pyelonephritis of dairy cattle associated with *Corynebacterium renale* infection.[25]

Favourable reports were made upon penicillin therapy in acute mastitis in sows,[26] in *Erysipelothrix rhusiopathiae* infection in turkeys,[27] and in localized laminitis in a mare.[28]

Miscellaneous medicines

Streptomycin.—A further preliminary report was received upon the use of this antibiotic in the treatment of bovine mastitis.[29] In experimental studies streptomycin gave promising results against the infectious agent incriminated in infectious sinusitis of turkeys,[30] the pathology of which condition was described in detail.[31]

Nisin.—Encouraging preliminary reports were received in the treatment of streptococcal and staphylococcal forms of bovine mastitis.[32]

Phenanthridium compounds.—In a trial involving 150 cattle with *Trypanosoma congolense* infection, dimidium bromide (phenanthridium compound 1553) gave a very high percentage of recoveries when administered intravenously in 2% solution at the rate of 8 mg. per 10 kg. live weight. There were 78% recoveries after a single treatment and the remainder after two or three treatments. Photosensitization did not occur when the drug was given by this route.[33]

'Antrycide.'—Field reports from Uganda are now to hand concerning the treatment by means of this new drug of *Trypanosoma simiae*, *T. congolense* and *T. vivax* infections.[34,35]

Paludrine.—Results from the treatment of experimental anaplasmosis in calves were inconclusive.[36]

Antihistamine compounds.—These substances have received considerable trial in veterinary practice.[37,38] Among the disorders successfully treated were 'blue nose' in horses[39] and laminitis in three species.[40]

Methyl silicone.—A proprietary preparation of a highly polymerized methyl silicone appeared to give a high percentage of recoveries when injected intraruminably or administered orally to cattle with 'bloat.' This agent increases surface tension and is believed to break down the foam that is formed in many cases of 'bloat.'[41]

Bisphenols and diphenols.—Laboratory tests demonstrated that several compounds of the dihydroxydiphenylmethane type possessed significant anticoccidial activity, and in feeding trials it was found that continuous administration of them gave protection against *Eimeria tenella* infection without interfering with the growth or thriftiness of 'broilers.'[42,43]

References

1 Gordeuk, S. and Thorp, W. T. S., *Bull. Pennsylvania Agric. exp. Sta.*, 1949, **510**, 1
2 Skjerven, O., *Norsk. Vet.-Tidskr.*, 1948, **60**, 412
3 Marthedal, H. E., *Med. Danske Drylaegefor.*, 1948, **31**, 394
4 Moore, E. N., *Cornell Vet.*, 1949, **39**, 223
5 Alberts, J. O. and Graham, R., *Amer. J. vet. Res.*, 1948, **9**, 310
6 Kiser, J. S., Prier, J., Futtorff, C. A. and Greene, L. M., *Poultry Sci.*, **37**, 257
7 Rosen, M. N. and Bischoff, A. I., *Cornell Vet.*, 1949, **39**, 195
8 Hilbert, K. F. and Kiser, J. S., ibid., 1948, **38**, 148

[9] Franklin, R. D., *Vet. Rec.*, 1949, **61**, 611
[10] Case, J. D., *J. Amer. vet. med. Ass.*, 1948, **113**, 348
[11] Wilson, J. M., *Vet. Rec.*, 1949, **61**, 12
[12] Lebovit, G. B., *J. Amer. vet. med. Ass.*, 1948, **112**, 453
[13] Schofield, F. W., *Canad. J. comp. Med.*, 1948, **12**, 305
[14] Schuhardt, U. T., Carroll, T. B., Rode, L. J. and Lacy, Helen, *Amer. J. vet. Res.*, 1948, **9**, 144
[15] Christian, A. B., *J. Amer. vet. med. Ass.*, 1948, **113**, 258
[16] Shanks, P. L., *Vet. Rec.*, 1949, **61**, 262
[17] Larsen, C. E., *Vet. Med.*, 1948, **43**, 231
[18] Cotton, C. M. and Swope, R. E., *Amer. J. vet. Res.*, **9**, 164
[19] Murnane, D., *Aust. vet. J.*, 1949, **25**, 85
[20] Zweig, J., *Vet. Rec.*, 1949, **61**, 811
[21] Carmichael, J., ibid., 886
[22] Benson, D. V., *J. Amer. vet. med. Ass.*, 1948, **113**, 160
[23] Murphy, J. M., *Cornell Vet.*, 1948, **38**, 156
[24] Edwards, S. J. and Taylor, J. I., *Vet. Rec.*, 1949, **61**, 780
[25] Arthur, G. H., ibid., 257
[26] Falster, L. B., *Manedsskr. Dyrlaeger*, 1948, **60**, 225
[27] Blaxland, J. D., Kershaw, G. F. and Howell, Deborah, *Vet. Rec.*, 1949, **61**, 350
[28] Crosfield, P., ibid., 53
[29] Schalm, O. W., *Cornell Vet.*, 1948, **38**, 186
[30] Hitchner, S. B., *Poultry Sci.*, 1949, **28**, 106
[31] Idem, ibid., 627
[32] Taylor, J. I., Hirsch, A. and Mattick, A. T. R., *Vet. Rec.*, 1949, **61**, 197
[33] Elst, O. V., *Bull. agric. Congo belge.*, 1948, **39**, 131
[34] Wilson, S. G., *Vet. Rec.*, 1949, **61**, 395
[35] Idem, ibid., 397
[36] Splitter, E. J., *J. Amer. vet. med. Ass.*, 1949, **114**, 224
[37] Kaplan, A. D., *Vet. Med.*, 1949, **44**, 82
[38] Rawson, G. W., *J. Amer. vet. med. Ass.*, 1949, **114**, 239
[39] Muir, R., *Vet. Rec.*, 1949, **61**, 139
[40] Kochan, W. F., ibid., 1948, **60**, 257
[41] Quin, A. H., Austin, J. A. and Ratcliff, K., *J. Amer. vet. med. Ass.*, 1949, **114**, 313
[42] Johnson, J. E., Mussell, D. R. and Dietzler, A. J., *Poultry Sci.*, 1949, **38**, 802
[43] Groschke, A. C., Davidson, J. A., Evans, R. J., Narotsky, S., Hawkins, P. A. and Reineke, E. P., ibid., 811.

FUNGICIDES (H. Martin)

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SEARCH for alternatives to sulphur and the copper compounds, which are still the most important fungicides used for the protection of foliage, is now gathering momentum and, in the United States, the dithiocarbamates are coming into practical use. The ferric and zinc dimethyldithiocarbamates, for which the common names Ferbam and Ziram have been proposed, seem especially suitable as substitutes for lime–sulphur in fruit-tree sprays.[1] Under English conditions however, neither has proved satisfactory for the control of apple scab. Marsh[2] pointed out that here it is usual to apply, at the most, two lime–sulphur sprays post-blossom whereas, in the United States, the fungicide is added to each of the long series of arsenical sprays required for the control of codling moth. The dithiocarbamates do not give adequate protection when applied only twice.

Disodium ethylene bisdithiocarbamate was shown by Horsfall and his co-workers[3] to be an effective protective fungicide, a property unexpected in a water-soluble compound. Heuberger and Manns[4] found that the protective properties were enhanced by the addition of zinc sulphate and lime to the solution. The explanation of this effect was traced by Barratt and Horsfall[5] to the formation of zinc ethylene bisdithiocarbamate, a reaction which proceeds in the presence of carbon dioxide. The zinc salt (Zineb) is now marketed in the States and is used as a substitute for Bordeaux mixture in the control of potato blight[6,7] Again, fortnightly applications are usual in the American potato fields, whereas here two applications only are made even where and when climatic conditions favour the spread of the disease. Large and Beer[8] found that the dithiocarbamate spray was less effective than Bordeaux mixture for blight control in Devon.

The comparative failure of the dithiocarbamate sprays in this country would suggest that they lack tenacity, the ability of the spray deposit to withstand weathering and dislodgment by growth extension of the foliage, and therefore require frequent application to maintain an adequate protection. This failing is common to most previous attempts to replace Bordeaux mixture or lime sulphur by, for example, copper oxychloride or elementary sulphur compounded to water-dispersible powders. For this purpose it is usual to incorporate a surface-active compound in the product to promote ready dispersion in water; this component survives in the spray deposit to redisperse the fungicide in rain droplets. Large, Beer and Patterson[9] found that, in the high Devon rainfall, the retention of Bordeaux mixture on potato foliage was twice that of sprays of equal copper content prepared from water-dispersible preparations of cuprous oxide or of copper oxychloride.

It is possible that hydrophobic properties contribute to the success of 2-heptadecyl glyoxalidine which, Marsh[2,10] found, in sprays containing 0·1%, controlled apple scab as effectively as lime–sulphur in the normal programme. The sprays caused no damage even to foliage of Stirling Castle, an apple variety so sensitive to sulphur sprays that it has gone out of commercial production. The fungicidal properties of the 2-alkyl- or 2-alkenyl-2-imidazolines (glyoxalidines) were discovered by Wellman and McCallan[11] and are protected by B.P. 598,927. They found that, for maximum fungicidal activity, the alkyl group should be of 13 to 17 carbon atoms, whereas derivatives with an 11 to 13 carbon chain were the most phytotoxic.

Organo-mercury derivatives, such as ethyl mercuric phosphate, methoxyethyl mercuric silicate, and phenyl mercuric acetate, remain the most effective fungicides for the seed treatment of cereals for they are highly effective in controlling the four most prevalent of the seed-borne cereal diseases. But for the protection of germinating seed, particularly in 'out-of-season' vegetable production when soil and weather conditions do not favour rapid growth, cuprous oxide is meeting competition from quinones. The first of this group to be commercially applied for seed protection was chloranil, tetrachloro-*p*-benzoquinone (Spergon), which was followed by Phygon, 2 : 3-dichloro-1 : 4-naphthoquinone.[12] The latter product was reported[1] to be useful for the treatment of vegetable

crops, though injurious to soya bean. Marsh[2] found it effective in protecting black currant from defoliation by *Pseudopeziza ribis.*

In the routine evaluation of organic compounds as fungicides, McGowan, Brian and Hemming[13] observed that many of the more promising were ethylenic compounds. Their preliminary results suggested that, in these compounds, fungistatic activity was associated with the tendency of the substituent groups to withdraw electrons from the double bond, e.g. the —C=C—NO_2 group as in ω-nitrostyrene. This systematic work has, as a long-term object, the elucidation of the activity of the powerfully fungistatic 'antibiotics' produced by soil organisms, a subject reviewed by Brian.[14]

References

1 Barss, H. P. *et al.*, U.S. Dep. Agric., Plant Disease Rep. Suppl. No. 176, 1948, p. 95
2 Marsh, R. W., *J. Pomology*, 1947, **23**, 185
3 Dimond, A. E., Houberger, J. W. and Horsfall, J. G., *Phytopathology*, 1943, **33**, 1095
4 Houberger, J. W. and Manns, T. F., ibid., 1943, **33**, 113
5 Barratt, R. W. and Horsfall, J. G., Bull. Conn. agric. Exp. Sta. 508, 1947
6 Davidson, R. S. and Rich, A. E., *Amer. Potato J.*, 1947, **24**, 35
7 Horsfall, J. G. and Turner, N., ibid., 103
8 Large, E. C. and Beer, W. J., *Ann. appl. Biol.*, 1946, **33**, 406
9 Large, E. C., Beer, W. J. and Patterson, J. B. E., ibid., 54
10 Marsh, R. W., *J. hort. Sci.*, 1948, **24**, 284
11 Wellman, R. M. and McCallan, S. E. A., *Contr. Boyce Thompson Inst.*, 1946, **14**, 151
12 tenHorst, W. P. and Felix, E. L., *Ind. Eng. Chem.*, 1943, **35**, 1255
13 McGowan J. C., Brian, P. W. and Hemming, H. G., *Ann. appl. Biol.*, 1948, **35**, 25
14 Brian, P. W., *Chem. & Ind.*, 1949, 391

CONTROL OF PLANT NEMATODES (B. G. Peters)

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DD mixture

In the last volume this section dealt mainly with the nematocidal use of some saturated mono- and dihalides of the simpler paraffins, leaving for present review DD mixture. Originally a by-product in the manufacture of plastics from petroleum, DD is a mixture of 1 : 3-dichloropropylene, 1 : 2-dichloropropane, and higher chlorides, of which the first (unsaturated) compound is thought to be mainly nematocidal. Since Carter[1] first reported nematocidal effects in 1943, about 100 references to it have appeared. Most of these relate to its use against 'root knot,' *Heterodera marioni*, in the U.S.A. but it has also been used with varying success against *Tylenchulus*, the citrus eelworm[2,3]; two cyst-forming species of *Heterodera*: *H. rostochiensis* on potato and tomato[4–13] and *H. schachtii* on sugar beet[14–17]; the root-rot eelworms, *Pratylenchus*, on tobacco, cotton etc.[18–24]; and the stem eelworm, *Ditylenchus dipsaci*, on rye.[25]

Jacks[26] and Tam[27] use a purified 50 : 50 mixture, and a method has

been protected for preparing 1 : 3-dihalogenopropylenes from the corresponding 1 : 2-propanes,[28] but otherwise the crude product is used: a heavy, thin, black liquid of pungent smell. Dorman and Minges[29] found that application as a water emulsion was better than injection of the neat liquid into soil, and Mullison[30] has used it, dispersed with Tween 80, in hydroponic cultures in a sand medium where 'root knot' was a major pest, but normally it is injected into soil. On a small scale a hand injector is used for spot injections but several drill-injection machines have been devised,[13,31,32] and a comparison shows the two methods equally efficacious.[33] The lateral spacing of spots and drills is important[5]: practice varies between 9 in. and 18 in.[15] with a large majority at 12 in.; alternatively, only the plant rows (before planting) may be treated[34] or the sites of future trees.[3] Similarly, depth of injection varies from 3 in. to 8 in. Schmidt[35] has shown that surface efficacy is reduced by deeper injection, and the top inch of soil is notoriously difficult to disinfect[15]: for this reason some kind of soil-sealing after injection is usual. This may take the form of treading (glasshouses),[36,37] rolling[9,13] or watering.[37–39] Godfrey[40] found watering better than rolling; Clayton and Ellis[41] found water sealing of little effect. In a large-scale test[13] comparing depths of 4 in. with 8 in., and rolling with no rolling, results varied at different sites and were nowhere very conclusive; on the average 8 in. was slightly better than 4 in., and rolling was beneficial.

Temperature, moisture and general soil condition are important factors bound up with the dispersion of the toxic vapour and the attainment of adequate concentrations over a sufficient time. Schmidt[35] has measured dispersion, through an indirect measure of concentrations at varying distances, at three moisture levels. McClellan *et al.*[42] have examined dispersion at six temperatures and two moisture levels over five different periods, using DD and three other fumigants against 'root knot' and fungi: their results favour high temperatures and wet (17–20%) soils. Field experience suggests the temperature limits 4·4–29·5° c.,[15,40] McFarlane[31] finding that more DD is needed above 29° c. Soils should be not too wet or too dry; DD has failed at moistures of 40% and upwards,[13] in peat soils. Such failures in peat soils[7] may thus be a moisture effect. It is generally agreed that soil should be in as good tilth as possible and free from plant residues.[15,40] The time of application usually varies from autumn to spring, the recent tendency being to favour autumn,[24,43] because of reduced phytotoxic effects[13,43] and also enhanced nematocidal effects.[13] Jeffers,[44] however, found no difference between the effects of spring and autumn injections.

Rates of application should vary according to soil type and to the other factors discussed, phytotoxic and/or economic factors usually setting an upper limit. Schmidt[35] holds that rate is unimportant above the level at which optimum dispersion occurs. McFarlane[31] found 200 lb. per acre adequate under favourable, but 400 lb. per acre poor under less favourable conditions. Using a geometric series of four application rates from 250 to 2000 lb. per acre, Thorne and Jensen[15] got best yields from the lowest rate. On the other hand, Van den Brande[25] found both yields and kills to be proportional to the rate, using four rates from 214 to 641 lb. per acre, but only the lowest was economic. Peters and Fenwick[13] also found

kills (after 4 weeks) and yield increases proportional to the rate at some sites: the rates were 200, 400 and 800 lb. per acre and both criteria reached, at best, about 50% at the top rate. Against the same (potato root) eelworm, Chitwood[6] in Long Island obtained a kill of 99·9% with 425 lb. per acre and the same at 1700 lb. per acre. Kincaid,[45] using 200 lb. per acre, got rather more than 1 lb. increase in yields of tobacco leaves from each 1 lb. of DD applied. At 300 lb. per acre annually for 3 years Ellis[46] found no complete eradication; this is general experience, at least, in the field.

There is no space to discuss 30 papers in which DD is compared with other nematocides (*see* especially Schmitt,[11] Simon,[17] McClellan *et al.*,[42] Jacks,[47] Christie,[48] and others.[5,8,23,46,49–52]) Most often the comparison has been with chloropicrin (than which DD is better, safer and cheaper[47,52]) and ethylene dibromide, on which experimental results differ.[24,30,42,53] Economically, its use has been justified in glasshouses[9,36] and in the field against 'root knot' eelworm[47]; otherwise it is debatable.[5,7,25] The criterion matters; Carter[52] has argued for yield as the best criterion while others have urged that nematocidal effects should be separately assessed,[13,24] Peters[10] getting yield increases in the absence of eelworms. This 'amendment' effect may be explicable in terms of soil microbiology and the nitrogen cycle.[27,54]

Of residual and side-effects, both good[15,41] and bad[15] effects on yield in the second year, or none,[12] have been found. Eelworm populations may be reduced yet more than recover on the following crop.[13,15,55] Taint has been recorded in carrots and strawberries,[56] and in potatoes with, as chemical correlate, an unknown fixed chlorine compound.[13] Fungicidal effects are slight[17,48] even at 1000 lb. per acre.[57] Phytotoxic effects vary: they may be absent 10 days after treatment[57,59] or present after 6 weeks,[36] and the effect may vary with season.[18,43] Reduced germination and root distortion may occur in beet[15,17] and beans are specially susceptible.[41,43,60]

References

[1] Carter, W., *Science*, 1943, **97**, 383
[2] Couranjou, A., *Fruits prim. Afrique Nord*, 1948, **18**, 374
[3] Foote, F. J. and Gowans, K. D., *Down to Earth*, 1948, **4**, 14
[4] Leiper, R. T., *Gdnrs. Chron.*, 1944, **116**, 208
[5] Chitwood, B. G. and Buhrer, E. M., *Proc. helminth. Soc. Wash.*, 1945, **12**, 39
[6] Idem, *Phytopathology*, 1946, **36**, 684
[7] Martin, G. C., *Nature*, 1947, **160**, 720
[8] Popham, W. L., *Agric. Chem.*, 1947, **11**, 30
[9] Robertson, D., *Scott. J. Agric.*, 1947, **26**, 160
[10] Peters, B. G., *J. Helminth.*, 1948, **22**, 117; ibid., 128
[11] Schmitt, C. G., *Phytopathology*, 1948, **38**, 23
[12] Peters, B. G., *J. Helminth.*, 1949, **23**, 73
[13] Peters, B. G. and Fenwick, D. W., *Ann. appl. Biol.*, 1949, **36**, 364
[14] Fletcher, H. L., Proc. Amer. Soc. Sugar Beet Technol. 4th Meeting, 1947, 413
[15] Thorne, G. and Jensen, V., ibid., 1947, 322; ibid., East Slope Reg. Mtg., 1947, 151
[16] Simon, M., *Publ. Inst. belge Amélior. Better.*, 1948, **16**, 241
[17] Idem, ibid., 1949, 1
[18] Brooks, A. N., *Rep. Florida agric. exp. Sta.*, 1947, 113
[19] Valleau, W. D. and Johnson, E. M., *Plant Dis. Rep.*, 1947, **31**, 427
[20] *Rep. Kentucky agric. exp. Sta.*, 1948, **60**, 32
[21] Kincaid, R. R. and Volk, G. M., Press Bull. Florida agric. exp. Sta. 1948, No. 655

[22] Anderson, P. J., Bull. Conn. agric. exp. Sta., No. 527
[23] Clayton, E. E. *et al.*, *Phytopathology*, 1949, **39**, 4
[24] Kincaid, R. R. and Volk, G. M., ibid., 11
[25] Brande, J. van den and Damme, J. van, *Meded. LandbouwHoogesch. Opzoek. Staat., Gent*, 1949, **14**, 135
[26] Jacks, H., *Orchardist N.Z.*, 1947, **20**, 8
[27] Tam, R. K., *Soil Sci.*, 1945, **59**, 191
[28] Fairbairn, A. W., U.S.P. 2,449,286
[29] Dorman, S. C. and Minges, P. A., *Proc. Amer. Soc. hort. Sci.*, 1947, **50**, 317
[30] Mullison, W. R., ibid., 1948, **52**, 467
[31] McFarlane, J. S., *Rep. Hawaii agric. exp. Sta.*, 1947, 146
[32] Tinguy, P. de, *Rev. hort. Algérie*, 1948, **52**, 37
[33] McFarlane, J. S. and Matsuura, M., *Phytopathology*, 1947, **37**, 39
[34] Nettles, V. F., Press Bull. Florida agric. exp. Sta., 1947, No. 638
[35] Schmidt, C. T., *J. econ. Ent.*, 1947, **40**, 829
[36] Dunn, E., *Grower*, 1949, **31**, 921
[37] Read, W. H., *Rep. exp. Res. Sta. Cheshunt*, 1947, **32**, 62
[38] Smith, W. P. C. and Harvey, H. L., *J. Agric. West. Aust.*, 1948, **25**, 283
[39] Linde, W. J. van der, *et al.*, *Fmg. S. Afr.*, 1948, **23**, 509
[40] Godfrey, G. H., *Progr. Rep. Texas agric. exp. Sta.*, 1947, No. 1062
[41] Clayton, C. H. and Ellis, D. E., *Phytopathology*, 1949, **39**, 583
[42] McClellan, W. D. *et al.*, ibid., 272
[43] Ellis, D. E. *et al.*, ibid., 590
[44] Jeffers, W. F., *Trans. Peninsula hort. Soc.*, 1948, **38**, 101
[45] Kincaid, R. R., *Phytopathology*, 1948, **38**, 570
[46] Ellis, D. E., Ext. Circ. N. Carolina agric. Coll., 1949, No. 337
[47] Jacks, H., *N.Z. J. Sci. Tech.*, 1949, [A], **30**, 123
[48] Christie, J. R., *Proc. helmith. Soc. Wash.*, 1947, **14**, 23
[49] Jacks, H., *N.Z. J. Sci. Tech.*, 1944, [A], **26**, 186
[50] Stark, junr., F. L., *Phytopathology*, 1944, **34**, 954
[51] Naude, T. J., *Fmg. S. Afr.*, 1947, **22**, 1054
[52] Carter, W., *J. Econ. Ent.*, 1945, **38**, 35
[53] Stark, junr., F. L. and Lear, B., *Phytopathology*, 1947, **37**, 698
[54] Pochon, J. and Lajudie, *Ann. Agron.*, 1948, **18**, 449
[55] Chitwood, B. G. and Feldmesser, J., *Proc. helminth. Soc. Wash.*, 1948, **15**, 43
[56] Watson, J. R. and Bratley, H. E., *Rep. Florida agric. exp. Sta.*, 1945, No. 57, 64
[57] Parris, G. K., *Phytopathology*, 1945, **35**, 771
[58] Idem, ibid., 1946, **36**, 408
[59] Foster, A. A. and Russell, J. C., *Rep. Florida agric. exp. Sta.*, 1947, 143
[60] Wilson, J. W., ibid., 204

ANALYSIS OF AGRICULTURAL AND HORTICULTURAL MATERIALS (J. H. Hamence)

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Fertilizers and feeding stuffs

A SURVEY of recent advances in the analytical chemistry of fertilizers has been made by K. D. Jacob.[1] This review covers the determination of both the major and minor fertilizing elements and also the acid- or base-forming qualities of fertilizers.

W. Leithe[2] has described a process for the determination of nitrate in fertilizers based upon the reduction of the nitrate to nitrite in acid solution by ferrous sulphate and subsequent titration with standard potassium permanganate.

A rapid method for the determination of potassium in fertilizers is described by G. Lejeune.[3] The method is a modification of the perchlorate method in which the interference by ammonia salts is avoided by the addition of formaldehyde. Available magnesium in mineral fertilizers has been investigated by L. J. Hardin, W. H. MacIntyre and H. S. Johnson, junr.[4] These workers describe a method for its determination by preliminary leaching with water and digestion of the insoluble with 2% citric acid. The magnesium is determined in the combined filtrates after removal of the calcium.

W. L. Hill *et al.*[5] have studied the citrate solubility of phosphoric acid present in phosphate-rock magnesium silicate glasses, and found that fineness of grinding has a more pronounced effect on the solubility than is the case with basic slags and α-phosphates.

In the field of feeding stuffs further collaborative work has been carried out by Berry[6] on catalysts for the determination of nitrogen in feeding stuffs: the work confirms that mercury is the best catalyst for this purpose. From time to time several different solvents have been proposed for the determination of true fat in fish meals; M. E. Stansby[7] recommends acetone for this determination. Methods of crude-fibre determination have been reviewed by K. Scharrer[8] who concludes that the Scharrer and Kurschner method is most suitable for routine work.

E. R. Armitage *et al.*[9] have described a modified method for the determination of lignin in plant material of high protein content, in which the protein in the defatted material is removed by trypsin-digestion after hydrochloric acid hydrolysis.

The determinatiin of lignin in plant materials has also been discussed in a series of papers by D. MacDougall and W. A. Delong.[10] A procedure is described to avoid losses due to hydrochloric acid treatment and to avoid high values due to preliminary drying of young plant material.

Soils

Many of the agricultural papers that have appeared during the period under review have been concerned with the analysis of soils.

The lime requirement of soils have received attention from a number of workers. Electrometric methods involving titration of soil suspensions in N-calcium acetate solution with N-sodium hydroxide solution to a definite p_H have been used by M. T. Litynski and F. Zimny.[11,12]

C. M. Woodruff[13] calculates the lime requirement by studying the effect of the soil on the p_H of a buffer solution; F. Todt[14] uses a solution of calcium hydroxide or calcium acetate instead of a buffer solution. An antimony electrode is recommended for speed in these tests by P. Lederle.[15]

Methods of extracting total phosphorus from soils have been reviewed by F. Burriel and V. Hernando.[16]

The determination of cation- and anion-exchange properties of soils have been investigated by A. Mehlich[17] using solutions of barium chloride buffered with triethanolamine. The method has been compared with the ammonium acetate method by W. J. Hanna and J. F. Reed[18] who found that the barium chloride method gave higher cation-exchange figures than the ammonium acetate method. A new strain of *Aspergillus niger*

has been developed for the determination of available potash and phosphoric acid by F. C. Gerretsin.[19] Urea was used as a source of nitrogen in these tests and the p_H of the soils was stabilized by the addition of calcium citrate.

Tommasi[20] has determined the so-called 'mineralizable' nitrogen in soils by treating the air-dried soil with water to give a 40% saturation and incubating at 30° c. for 21 days. At the end of the period the nitrate and ammonia present are determined, nitrate by the phenoldisulphonic acid method and ammonia by direct nesslerization, after suitable treatment of the soil extract.

The efficiency of the lactate method for the determination of easily soluble or available phosphoric acid and potash in soils has been compared with the seedling method by P. Lederle[21] but comparable results were not obtained particularly with potash.

M. V. Tracey[22] has modified the method of Lefevre and Tollens[23] for the estimation of uronic acids in soils. The dry soil is heated with 12% hydrochloric acid in a sealed tube for 5 hr. in boiling toluene. The carbon dioxide evolved is measured in the Van-Slyke–Niell apparatus.

V. Burriel and V. Hernando[24] have studied the substances which are likely to interfere in the colorimetric determination of phosphorus in soil extracts. They recommend heating with concentrated sodium sulphite solution to avoid iron interference and p_H adjustment to avoid interference from silica and titanium. When large amounts of silica are present treatment with perchloric or sulphuric acid is necessary.

The factors governing the estimation of easily reducible manganese in soils have been discussed by H. G. Dunn, P. T. G. Mann and S. G. Heintze.[25]

Plant material

A new method for the determination of boron in plant material has been described by C. M. Austin and M. C. Hargue[26] based upon ignition of the material with barium hydroxide, extraction of the boron from the residue with acetic acid and subsequent colorimetric determination with *p*-nitrobenzene-azo-1 : 8-dihydroxynaphthalene-3 : 6-disulphonic acid, Chromotrope B.

Mineral deficiencies in plant tissues have been investigated by D. J. D. Nicholas[27] by extracting the plant material with Morgan's reagent and estimating the elements colorimetrically or turbidimetrically in the extract. In this manner threshold values for deficiency or toxicity have been established. The same worker[28] has also compared the results obtained by these rapid tissue tests with ash analyses and reports satisfactory agreement at deficiency levels but agreement not always good at higher levels.

C. H. Hills and H. N. McKinney[29] have described a process for the determination of tobacco-mosaic virus protein in plant extracts depending on the precipitation of the virus protein at its isoelectric point p_H 3·4.

Insecticides and fungicides

P. R. Averill and M. V. Morris[30] have described a process for the determination of parathion (*O-O*-diethyl-*o-p*-nitrophenyl thiophosphate)

residues on plant material involving extraction with benzene, evaporation, reduction to amine, diazotization and coupling with *N*-(1-naphthyl)-ethylenediamine to form a coloured compound.

The yellow coloration obtained when the acetone washings from seeds are treated with anhydrous diethylamine forms the basis of a test for residual tetrachloro-*p*-benzoquinone on seeds devised by H. P. Burchfield and G. L. McNew.[31]

Optical and polarographic methods have been employed by D. K. Gullstrom and N. P. Burchfield[32] to augment the sedimentation pipette method in the study of the particle size of organic fungicides and insecticides or dilute suspensions.

A qualitative test for residual chloranil (Spergon), used as a seed disinfectant, based upon the treatment of the seeds with acetone containing a small amount of aniline when a violet colour is obtained, has been described by K. G. Bergner, E. B. Bremanis and H. Sperlich.[33]

M. K. Alessandrine[34] reports on a method for the estimation of residual DDT. In this method the usual benzene extraction is followed by nitration after evaporation. The nitro compound is finally extracted with benzene and treated with N-alcoholic potash when a violet coloration is obtained ; the colour changes to orange on standing.

References

1 Jacob, K. D., *Analyt. Chem.*, 1949, **21**, 208
2 Leithe, W., ibid., 1948, **20**, 1082
3 Lejeune, G., *C.R. Acad. Sci., Paris*, 1948, 227, 434
4 Harden, L. J., MacIntyre, W. H. and Johnson, junr., H. S., *J. Ass. off. agric. Chem., Wash.*, 1948, **31**, 405
5 Hill, W. L., Ward, F. W., Armiger, W. H. and Jacob, K. D., ibid., 387
6 Berry, R. C., ibid., 617
7 Stansby, M. E., ibid., 606
8 Scharrer, K., *Z. Pfl. Ernähr. Düng.*, 1948, **40**, 54
9 Armitage, E. R., Ashworth, R. de B. and Ferguson, W. S., *J. Soc. chem. Ind.*, 1948, **67**, 241
10 MacDougall, D. and Delong, W. A., *Canad. J. Res.*, 1948, **26B**, 457
11 Litynski, M. T. and Zimny, F., *Bull. Int. Acad. polon. Sci.*, 1948, I (6A), 24
12 Idem, *C.R. Sci. Math. nat. Acad. polon*, 1948, 7
13 Woodruff, C. M., *Soil Sci.*, 1948, **66**, 53
14 Todt, F., *Z. Pfl. Ernähr. Düng*, 1946, **37**, 222
15 Lederle, P., ibid., 1948, **41**, 6
16 Burriel, F. and V. Hernando, *An. real. Soc. esp. Fiss Quim.*, 1949, **45B**, 25
17 Medlich, A., *Soil Sci.*, 1948, **66**, 429
18 Hanna, W. J., Reed, J. F., ibid., 447
19 Gerretsin, F. C., *Analyt. chim. Acta*, 1948, **2**, 782
20 Tommasi, G., *R.C. Staz. Chim. agrar. spe.*, 1939, **352**, 19
21 Lederle, P., *Z. Pfl. Ernähr. Düng.*, 1947, **39**, 202
22 Tracey, M. V., *Analyst*, 1948, **73**, 554
23 Lefevre, K. U. and Tollens, B., *Ber. dtsch. Chem. Ges.*, 1907, **40**, 4513
24 Burriel, F. and Hernando, V., *An. real. Soc. esp. Fiss. Quim.*, 1948, **44B**, 329
25 Dunn, H. G., Mann, P. J. G. and Heintze, S. G., *J. agric. Sci.*, 1947, **34**, 17
26 Austin, C. M. and McHargue, J. S., *J. Ass. off. agric. Chem., Wash*, 1948, **31**, 427
27 Nicholas, D. J. D., *A.R. Agric. Hort. Res. Sta., Bristol*, 1948
28 Idem, *J. hort. Sci.*, 1948, **24**, 771
29 Hills, C. H. and McKinney, H. N., *Phytopathology*, 1942, **32**, 433
30 Averill, P. R. and Morris, M. V., *Analyt. Chem.*, 1948, **20**, 753
31 Burchfield, H. P. and McNew, G. L., *Phytopathology*, 1948, **38**, 299
32 Gullstrom, D. K. and Burchfield, H. P., *Analyt. Chem.*, 1948, **20**, 1174
33 Bergner, K. G., Bremanis, E. and Sperlich, H., *Suddtsch. apoth. Ztg.*, 1948, **88**, 329
34 Alessandrine, M. E., *Ann. Chim. appl., Roma*, 1948, **38**, 414

CONTROL OF PEST INFESTATION

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Some economic aspects of insecticides

IN the earlier stages of the introduction of chlorinated-hydrocarbon insecticides it was generally supposed that the formulations based on naturally occurring plant derivatives such as pyrethrum and rotenone would occupy an increasingly smaller fraction of the world insecticide consumption. At that time it appeared as if the greater stability and cheapness of the new insecticides might make the large-scale production of insecticides of vegetable origin economically impracticable.

Some of the disadvantages of the chlorinated hydrocarbon insecticides were rapidly manifested, in particular their relatively slow speed of action; others, notably the too effective control of insect parasites and predators and the development of resistant strains of insects, have become evident more recently.

DDT particularly has given disappointing results against the many hemipterous insects, which feed by sucking plant juices rather than by chewing plant tissue. Some half-dozen chlorinated organic derivatives have since been developed, any one of which has special uses; most are more effective than DDT against the two main orders of sucking insects, the hemiptera and the homoptera; generally, however, these insecticides have many uses in which they have a toxicity to insects comparable with that of DDT itself. The relative effectiveness of these new substances depends very largely on the methods of application and, where their use is against pests of crops, on the agricultural and climatic factors involved. The complexity of the situation is such that the capacity of the world's economic entomologists to evaluate the relative merits of new insecticides is rapidly approaching saturation. It is to be expected that for some time the greatest practical benefits will be derived from the extended application of existing knowledge rather than from new developments.

Meanwhile, pyrethrum and rotenone have steadily regained the interest temporarily lost, and with the great expansion in the general uses of insecticides they are being produced in much greater quantities than before.

Rotenone retains a limited use, mainly against aphis, in the form of derris dusts and sprays, whereas the high rate of paralysis conferred by the pyrethrins has led to their extensive use in household and veterinary fly-sprays, both alone and in combination with other and more stable substances.

The production of pyrethrum flowers in East Africa has greatly expanded in recent years and the quality of the product, in terms of the content of active ingredients, is steadily improving. The price, however, remains high in comparison with the synthetic insecticides and where the quality of the flowers is poor the crop tends to be uneconomical.

Partly for this reason two pyrethrum stations in Ceylon[1] have been closed down recently. From other Ceylonese stations, however, good quality flowers continue to be exported.[2]

The fact that the bulk of the active ingredients occurs in the flower achenes has led to the exploration of the possibility of shipping this part of the flower only, to avoid the heavy cost of transport of the whole baled flowers. If practicable these achenes would be baled under the trade name of 'Florax.'[3] The deterioration of the achenes relative to the whole flowers has been given some attention.[4,5] A recent improvement in baling the whole flowers consists in replacing the sisal 'scrim' by paper as a bale covering,[6] and spraying the bale with an antioxidant before covering; the extraction of the active ingredients before shipment would constitute yet a further improvement.

An event of great theoretical interest is the announcement of the completed synthesis of esters of similar constitution to the pyrethrins.[7] This synthesis was accomplished by La Forge and his associates, as the result of the convergence of two lines of research pursued by La Forge's team and one led by Harper.

The production of synthetic pyrethrins on a commercial scale will inevitably take a considerable time to develop,[15,16] although a small-scale production of the allyl homologue of cinerin is reported; but if the process proves practicable on a large scale it might eventually result in the production of an insecticide having the desirable properties of the pyrethrins, so that its use could be largely extended. In any case there is likely to be a demand for the natural product for some considerable time to come, and the abandonment of pyrethrum plantations might well result in an acute shortage of the insecticide for a period. There is, of course, no guarantee that the synthetic production of the pyrethrins will be economically practicable, particularly if the East African industry pursues an active policy of cutting down transport and other production costs. Meanwhile, largely owing to increased demand, the price of pyrethrum rises.[8] New diseases of pyrethrum flowers do occur, but are not usually very widespread or serious: an example is bud rot due to the fungus *Ramularia bellunensis*.[10]

Another factor of current importance is the swing towards the use of insecticides which are proved not to be toxic to warm-blooded animals.[11,12,13] In dairies and cattle byres, for example, the use of DDT has been virtually abandoned in the United States. In the earlier stages of the introduction of the halogenated hydrocarbon insecticides their toxicity to man was perhaps underestimated. Recently, however, the pendulum has swung the other way; where previously great stress was laid on the halogenated-hydrocarbon content of certain commercial products a perusal of advertising material, in the United States particularly, gives the impression at present that the complete absence of such insecticides is a point likely to win the public favour. It is hard to believe that the rapidity and extent of this change can be related solely to the scientific appraisal of the toxicity of the insecticides in question. Doubtless there are fashions even in insecticides.

One of the factors which has been found objectionable in the widespread use of benzene hexachloride is the odour associated with it. It is reported

that this odour has been substantially removed in the course of increasing the proportion of the insecticidally active isomer to 97% by partition chromatography, though this method is hardly likely to be easily scaled up to the production level.[9]

Development in the synthesis of the pyrethrins

The successful synthesis of insecticidal esters referred to previously, has, as its background, a timely and comprehensive, though not generally accessible, review of the chemistry of the insecticidal constituents of pyrethrum flowers by S. H. Harper[17,18]: this supplements a previous review by the same author[19] and a similar review by West.[20] Much of the earlier degradative work on the structure of the insecticidal esters was carried out in the absence of adequate information as to the number of active ingredients present. Considerable confusion existed as to the differences between the side-chains of the different molecules and their position of attachment to the cyclic keto-alcohols which form one component of the esters. In the earlier work of Staudinger and Ruzicka, there were thought to be two constituents in which a common alcoholic component 'pyrethrolone' was attached to one of two monoterpinic acids, chrysanthemum monocarboxylic acid and the monomethyl ester of chrysanthemum dicarboxylic acid. Other terpinoid acidic components have been reported, but are of doubtful authenticity.

The ester with the monocarboxylic acid was termed 'pyrethrin I' and that with the dicarboxylic acid component 'pyrethrin II.'

Some 20 years after this work fractional distillation of derivatives of 'pyrethrolone' showed that this component was itself heterogeneous and eventually six components were isolated, being the D- and DL-forms of three different keto-alcohols. By direct distillation of 'pyrethrolone' itself, West[21] was able to show that the DL-compounds were produced during the isolation of the pyrethrolone derivatives, a racemization process giving rise to artefacts. The three D-compounds have been described as two pyrethrolones proper, the *cis*- and *trans*-isomers of 3-methyl-2-penta-2 : 4-dienyl*cyclo*pent-2-en-4-olones, the isomerism occurring about the double bond in the 2-position and a 3-methyl-2-but-2-enyl*cyclo*pent-2-en-4-olone to which the name 'cinerolone' was given.

These three alcoholic components would give six 'pyrethrins' when esterified with the two acid components, so that much of the work done to elucidate the nature and position of the side-chains on the pyrethrolones before the heterogeneity was established is, as S. H. Harper[17] points out, of uncertain value. Further complications arise since considerable proportions of the crude 'pyrethrin I' assembly, as normally obtained, consists of esters of the pyrethrins with palmitic and linoleic acids. The toxicity of such esters appears not to have been investigated. In addition, Kuhn–Roth oxidation of the pyrethrolones gives terminal methyl values considerably higher than those expected on the basis of one methyl group per alcoholic residue. As such terminal methyl values are often rather lower than higher than the true values, it has been suggested that dihydropyrethrolones occur, with relatively more saturated side-chains. Ozonolysis of D-cinerolone by S. H. Harper[17] has given small quantities of formaldehyde in addition to the expected acetaldehyde.

The presence of the former compound could be interpreted as being derived from a but-3-enyl isomer of cinerolone, in addition to the major component, the but-2-enyl isomer. Since both *cis* and *trans*-pyrethrolone occur naturally, and similar isomerism is obviously a possibility with cinerolones, it was of interest to assign the appropriate configuration to the latter compound. This work[22] was facilitated by a reaction undergone by cinerolone but not by pyrethrolone, in which the hydroxyl group is replaced successively by chlorine, and then by hydrogen to give cinerone (3-methyl-2-but-2-enyl*cyclo*pent-2-enone).

The *trans*-isomer of methyl dec-8-en-2 : 5-dione-4-carboxylate, obtained from *trans*-crotonaldehyde, was cyclized by aqueous alkali to give the *trans*-cinerolone, whose semicarbazone and phenylhydrazone depressed the melting points of the corresponding derivatives of the natural compound. A further synthesis from furan, also by Harper[17] and his co-workers, provides independent confirmation of the *trans*-configuration of the synthetic ketone, which has a higher melting point for its semicarbazone than that of the natural compound. Naturally occurring cinerone, and hence cinerolone, are thus assigned the *cis*-configuration. La Forge, Green and Gersdorff[23] have synthesized cinerone from a *cis*–*trans* mixture of but-2-enes *via* the corresponding crotyl chlorides. It is considered that the *cis*-isomer would predominate during this synthesis, and indeed the semicarbazone of the resultant cinerone raises the melting point of that of the naturally occurring product.

The work leading to the evaluation of the ring structure and position of attachment of the side chain of pyrethrolone and cinerolone is described in detail by Harper in his review; he also describes more recent work leading to the allocation of the 4-position of the ring to the point of substitution of the hydroxyl group.[24,25,27,28,29] It is also inferred that since the pyrethrolones and cinerolone are all dextro-rotatory their stereochemical configuration about the asymmetric 4-carbon atom may be the same.

Attempts to synthesize cinerin I have, in the past, broken down when the synthetic cinerone is used as a starting material. The dihydroketone, like the tetrahydropyrethrone, can be converted by means of *N*-bromosuccinimide to the 4-bromo derivatives, and these in turn esterify with chrysanthemum monocarboylic acid (as the silver salts in benzene solution), to give completely synthetic racemic stereoisomers of dihydrocinerin I and tetrahydropyrethrin I respectively.[28]

The attack of *N*-bromosuccinimide on the side-chain, however, prevents this method from working with the non-hydrogenated compounds,[23] which would lead to insecticidally active esters.

The successful approach of La Forge *et al.*[25,30,31] began by preparing DL-2-alkenyl-3-methyl*cyclo*pent-2-en-4-olones from pyruvaldehyde by condensation with the sodium salts of β-keto-acids. On esterification with chrysanthemum monocarboxylic acid these products give a series of substances closely related to cinerin I. The allyl derivative of cinerin I, i.e. with an allyl side chain attached to the cinerolone ring, has been claimed to be more toxic than any other derivative, natural or synthetic.[7]

Harper[18,26] has pointed out that the nomenclature of the pyrethrum analogues requires reconsideration and suggests that a system of names

similar to those of the penicillin derivatives would be suitable. The main structure or 'stem' of the molecule would have the suffix -rethrin, with the suffix I or II to denote the mono- and di-carboxylic acid esters respectively: this is logical, if tentative methods for detailed work and trade purposes are discussed, and the scheme appears to be well worthy of general adoption. As an example, the new toxic allyl analogue of the cinerins would be (+)allylrethronyl (+)-*trans*-chrysanthemate, or 'allylrethrin I' for less formal occasions.

Determination of the active constituents of pyrethrum flowers

In the past a considerable number of methods for the quantitative estimation of the active ingredients of the pyrethrum flowers, and of extracts prepared from them, have been proposed. Of these methods, chemical, biological and physical in nature, none has been particularly satisfactory. A general method for extracts containing DDT, the pyrethrins and sesame oil has been offered by Canneri.[32]

The physical assay depends on the strong absorption of ultra-violet light at 230 mμ. by the various constituents.[33] This method cannot be made of great accuracy, partly because of the non-specificity of absorption at such wavelengths, and partly because the action of ultra-violet light of the appropriate frequency results in the decomposition of the pyrethrins. Nevertheless, this method has the great advantage that numerous routine assays can rapidly be made by it with an accuracy sufficient at least for grading flowers in East Africa.[34]

The many chemical methods proposed have two features in common. One of these is their dependence on the estimation of the chrysanthemum carboxylic acids formed by saponification of the active esters and the other is the presence, in the various prescribed forms of analysis, of steps whose nature and duration are somewhat arbitrarily fixed.[35]

Both these features militate against the precision of the chemical assays; W. Mitchell[36] has reported an investigation into the extraction of substances other than the pyrethrins from the ground flowers which after hydrolysis give the reactions of the carboxylic acids. It was earlier proposed to substitute *n*-hexane for the less homogeneous light-petroleum fractions previously used.[35] Subsequent work showed that the type of solvent was of less importance than the temperature at which extraction was carried out in determining the fiducial content of 'pyrethrins' in the flowers. When the extraction is done by cold percolation, the apparent pyrethrins contents are almost independent of the nature of the solvent, but if the extraction is carried out in a Soxhlet apparatus the value obtained depends on the boiling range of the solvent used.

Of particular significance is the fact that if a low-boiling light petroleum (40–60° c.) is used to extract the ground flowers in a Soxhlet apparatus almost all the active ingredients are removed. The residual marc, if extracted further with chloroform (b.p. 59° c.) or light petroleum (75–95° c.) gives an extract which assays chemically for a further 41 and 3% of 'pyrethrins' respectively. This additional quantity of reactive substances was, however, found to be insecticidally inactive, so that the result obtained by this method was erroneously high—seriously in the case of the chloroform extract.

It is only the 'pyrethrin II' constituents whose apparent abundance in the flowers is thus inflated; that of the 'pyrethin I' aggregation is relatively unaffected by the temperature of extraction.

The suggestion has repeatedly been made[36] that the 'pyrethrins' content of flowers and extracts should be based on the content of 'pyrethrin I' (pyrethrin I plus cinerin I, both in the narrow sense).

Added force has been lent to this suggestion by Harper,[6] who points out that chrysanthemum monocarboxylic acid normally separated from the dicarboxylic acid by steam distillation from mineral acid solution in both the Seil and Ripent methods of analysis, can undergo a facile acid-catalysed addition of water.

After this addition, the hydroxy-acid formed is not volatile in steam and its disappearance from the acid fraction assayed as 'dicarboxylic acid' is associated with a corresponding spurious increase in the 'monocarboxylic acid' titration values.

Such observations are supported by a study of the accuracy of the various methods of analysis, using the pure chrysanthemum acids,[37] and it is suggested that the Wilcoxon–Holoday method of extracting the monocarboxylic acid by cold light petroleum would greatly reduce losses due to hydration of this acid.

It may be noted here that a purely quantitative test for the pyrethrins has been proposed[38] but it is not at the moment clear how specific and sensitive this test may be, nor upon what reaction it is based. Such a test might well be useful now that mixed insecticides are becoming more freely used.

It will be observed from what has been said above that biological assays are complementary to chemical assays, and that conclusions drawn from the latter are likely to be dangerous if not related to the toxicity of the sample under assay.[39]

In the past, the products of careful and painstaking chemical research have been examined by biological methods of low sensitivity, and frequently under conditions where the quantitative estimates of relative potencies of samples are almost valueless. An attempt has been made to improve the assay of pyrethrins by means of crawling insects, so that the precision of relative-potency estimates can now compare favourably with those obtained by chemical methods. The widespread use of the Peet–Grady system, in which flying insects (houseflies) are used as test insects has contributed not a little towards the low standard of biological assays. This system is one of great complexity and the methods of using it involve tacit hypotheses which are in many cases unfounded and lead to results which are not only quantitatively, but occasionally even qualitatively, in error.

Unless drastically reconstructed the Peet–Grady method is capable, at best, of only low precision; but its extensive semi-official adoption in U.S.A. has rendered it of sufficient importance to require further study, the results of which are now becoming available.[41–43]

It may be noted that until active pyrethrins and cinerins have been made available in a pure form for calibrating the analyses, neither chemical nor biological assays can be studied from the point of view of

their accuracy. Biological assays will give estimates of relative potencies of preparations, and an estimate of the precision of the assay is an integral part of the experiment. Chemical assays have been calibrated absolutely in terms of the chrysanthemum carboxylic acids actually determined but as Mitchell's work shows, there is no guarantee that even that part of the 'pyrethrin II' (in the broad sense) extracted by cold solvents is wholly insecticidally active; in the absence of pure active compounds in sufficient quantity, the hypothesis that they are so active cannot be tested, and it cannot lightly be assumed that the determined acids are quantitatively derived from active material.

Investigations of the precision of chemical assays frequently suffer from inadequate attention to the sources of variation involved, so that many such sources, which with improved experimental design could be validly segregated, contribute to the apparent experimental error.

One such component of variation in pyrethrum analyses has been the difference between the mean results of replicated determinations made by one worker in one laboratory and corresponding results obtained by another worker in a different laboratory. The magnitude of these differences in comparison with the reproducibility within a given environment has given rise to much disagreement, the true nature of which is brought out by a collaborative determination of the factor for 'pyrethrin I' (in the broad sense) in the Wilcoxon–Holoday mercury-reduction method.[44] Two of the conclusions resulting from this investigation were, first, that the appropriate factor should be 5·7 times the volume in ml. of 0·01M-potassium iodate solution consumed in the eventual iodometric titration instead of 4·4 as originally put forward. This first conclusion is in agreement with those of American workers published some time before. The second conclusion was that the various arbitrarily standardized steps in the analysis must be laid down unambiguously and rigidly if reproducible results are to be obtained.

Partly as a result of this latter recommendation, a world-wide collaborative scheme of analysis was instituted and the conditions for the analysis of pyrethrum flowers by the three most commonly used methods are laid down.[35,45]

Vegetable insecticides other than pyrethrum.—Of the insecticides of vegetable origin other than pyrethrum, a good deal has been written since the last report was prepared on the chemical constitution and field trials; that a considerable number of such substances are available in different parts of the world is revealed in a survey by Tattersfield *et al.*,[46] in which some interesting tests are recorded of extracts of plants enjoying local reputations as insecticides.

Of 19 British plants examined, only the fruits of the spindle tree (*Euonymus europaeus*) showed noteworthy toxicity, and that scarcely sufficient to warrant comparison with pyrethrum or derris. The fairly widespread belief that tomato foliage has insecticidal properties is not supported by critical work. The seeds of *Milletia pachycarpa* were found to be appreciably toxic and the suggestion is put forward that selection for increased yield of insecticide might be worth while, since the currently used fish-poison legumes, such as derris and lonchocarpus, though at present more potent, require that their roots should be harvested

to obtain the insecticidal material, whereas *Milletia* presents the easier task of harvesting the seeds.

Massee[47] has given recommendations for the use of nicotine and derris in horticultural insect control, and a number of descriptions of the comparison of the extracts and dusts of *Sabadilla* and *Ryania* against various chlorinated-hydrocarbon insecticides. The results of these investigations are conflicting,[48] and the particular pest controlled appears to be of particular importance in determining the relative toxicity, though doubtless important differences in the methods of application of the insecticide are also responsible for the widely discrepant results.

The toxicity of nicotine to workers applying it as a concentrate constitutes a serious hazard, the avoidance of which has been discussed by Harris and Davies.[51]

Jacobson,[52] has extracted an active ingredient from the roots of pellitory, *Anacyclus pyrethrum*, which was stated to possess about half the toxicity of pyrethrum itself to houseflies, with a good knock-down action. The active principle, pellitorin, was shown to be the *iso*butylamide of *n*-nonadiene-1-carboxylic acid[53] with double bonds at the 1 : 2- and 5 : 6-positions.[52]

Of the four possible *cis-trans* isomers of pellitorin, the *cis-cis* isomer, a liquid, has been synthesized,[54] whereas another prepared by Jacobson[55] has been shown to be the *trans-trans* isomer.[56] Neither of these compounds is appreciably toxic, nor do they share with the natural product the effect of inducing salivation when placed on the tongue.

This salivation effect is a property of the *trans-cis* derivative, but again this substance is not as toxic to houseflies as the natural product. It is considered, therefore, that the isomer occurring in pellitory roots must be the *iso*butylamide of *n*-nona-*cis*-1-*trans*-5-diene-1-carboxylic acid.[56] This structure is unusual in naturally occurring acids, however, and the order of melting points of the various isomers is somewhat anomalous, so that positive identification awaits the synthesis of the *cis-trans* isomer.

The rapidity with which in recent years the active ingredients of plants having insecticidal properties have been isolated, identified and in many instances synthesized is noteworthy. The interest shown by organic chemists in this field is of value not only in the perennial problem of the relation between chemical constitution and biological activity, but also in removing from the biological work a class of difficulties associated with the use of impure materials of unknown composition.

The same authors[57] have synthesized herculin, following the investigations of Jacobson.[58] This substance shares with pellitorin a rather pungent odour and is isolated from the bark of the southern prickly ash (*Xanthosylum clavaherculis*). The active principle of *Ryania speciosa* has been studied by Rogers *et al.*,[59] and given the name ryanodine. The low toxicity of ryanodine to warm-blooded animals is stressed by Heal.[60] A series of structural investigations by means of syntheses has been progressing steadily, both into that of rotenone itself,[61] and of its analogues.[62]

The fact that the toxicity of derris and lonchocarpus, two major sources of rotenone, cannot be properly evaluated on the basis of their rotenone content alone is becoming increasingly well demonstrated.[63]

Derris, of equal rotenone content to lonchocarpus, is more toxic to insects and this phenomenon is associated with the presence of resinous products in the derris root. The suggestion has been made that a separate system should be followed when assessing the value of the two sources of rotenone.[64]

A rapid method of extracting rotenone and allied substances from derris roots has long been required by those engaged in the analysis of these products, and this need appears to be satisfied by the method of Hagemann.[65] A review of the recent developments in the analysis of rotenone has been given by Spurs.[66] The effects of various methods of drying after the roots have been harvested has been investigated.[67]

Two vegetable insecticides from Russian sources have been discussed, but although one, from the flowers of *Matricaria inodora*, is said to be at least as good as pyrethrum flowers, the value of these products is rather hard to assess.[68,69] From Holland comes news of the insecticidal properties of the seeds of *Pachyrrhizus enoscis*, and indeed, examples of potentially useful plant products might be multiplied many times.[70]

Synergists.—A limited amount of information on compounds intended to act as synergists with other insecticides has been produced since the last report. Possibly the 'screening' of new compounds for synergistic action has exhausted the supply of potentially useful subjects; the inefficiency of large-scale 'screening' tests is demonstrated by the report[71] that some 3800 such compounds have been examined in the United States in this way, and of these only five were found to be worthy of further investigation.

This situation recalls that during the war, when many thousands of potential mosquito-repellants were sorted out at Orlando, Florida, none were found superior to those already known to be valuable. An improved method of extracting the well-established pyrethrum synergist sesamin from crushed sesame seeds has been put forward; methanol is used instead of a less polar solvent.[72]

In an extension of work reported in the last Annual Report, it has been found that sesamin and *iso*butylundecylenamide have essentially the same mode of action in oil-base films as in water-base sprays, but there is evidence that piperonyl butoxide and piperonyl *cyclo*hexenone, known by the trivial name of 'piperonyl cyclonene,' differ from the older synergists appreciably. Piperonyl butoxide appears to increase the toxicity of the pyrethrins up to a maximum factor of nine at a molecular ratio of about five parts synergist to one of pyrethrins, the factor decreasing to a constant level with further addition of the synergist.[73] With the two older synergists, however, the toxicity rises to a maximum at a molecular ratio of 3 : 1 which does not decrease at higher ratios of synergist.[74] Clearly some intriguing physico-chemical problems await investigation in this field.

As noted in last year's Report, many supposed examples of synergism with other insecticides do not differ significantly from the additive toxicity of the components of a mixture. One undoubted case of synergism between DDT and a number of quinonoid derivations has, however, been reported.[75] From the figures given, it may be estimated that 5% (w/w)

of β-methylanthraquinone increased the toxicity of DDT films by a factor of very nearly two.

Protection of bagged grain.—Beckley[76–79] has observed that bagged grain can be effectively protected against infestation by grain weevils by adding small quantities of pyrethrum powder. A similar method has been employed for flour-bags.[82] This form of protection can last for quite a long time: it shows the comparative stability of the pyrethrins when protected from the action of light. Bovingdon[80] has pointed out that hexachloro*cyclo*hexane has the same protective action on bagged grain, and claims that this substance is more toxic at 0·5 p.p.m. than the pyrethrins at 27 p.p.m. Although the low concentration of hexachloro*cyclo*hexane is free from health hazards, the taint left by admixture with the insectide may be a factor of importance in European countries, though it may not be appreciable in comparison with the flavour imparted to stored grains by certain tropical storage practices.

DDT used as both 5% dusts and as a water-miscible powder in a spray[81] has been employed for controlling rice weevils and grain moths in stored maize, and has also given satisfactory results. Probably the determining factor in the preferential use of one of these three substances will prove to be availability at the site of storage, particularly when the conditions are such that fumigation is difficult to carry out successfully.

Deleterious action of insecticides

The possible deleterious effects of an insecticide may apply to the host or substrate of the insects, to their parasites, to beneficial insects, or to those applying the insecticides or consuming the treated product.

Experiments at Rothamsted reviewed in last year's Report show that both DDT and benzene hexachloride are phytotoxic under certain circumstances. Curcurbits in particular were affected,[83] but DDT appeared less toxic than hexachloro*cyclo*hexane. Kostoff[84] has also reported that the latter substance has deleterious effects on the processes of cell division in plants.

Direct application of DDT and benzene hexachloride to roots of seedlings and small plants is frequently tried. Benzene hexachloride is generally much more successful in controlling or in reducing damage by pests but is also more phytotoxic: cf. Stilt and Eide,[86] who found that the damage was increased by phosphoric acid in the starter solution. According to Smith[87] both DDT and benzene hexachloride are surprisingly stable in acid and even in alkaline soils, in one instance 95% of DDT and 80% benzene hexachloride being recoverable 18 months after application. It seems unlikely that this could apply to a wide range of soils. When the insecticide is mixed with the soil or applied to the roots irradiation is substantially absent.

The suggestion has been made[85] that hexachloro*cyclo*hexane may be non-toxic to plants in itself, but may break down to give toxic residues. Of these substances the most likely to cause damage is 1:3:5-trichlorobenzene, which is known to be produced from the insecticide under field conditions. This breakdown product is active in gaseous form and in such low concentrations that its use as a weed killer is suggested.

The importance of impurities in causing plant damage is brought out by the work of Bertossi and Ciferri[88] on the effect of γ-benzene hexachloride and various impurities on the root system of seedlings of *Lupinus albus*. On the one hand the less insecticidally important isomers produce relatively little damage; on the other hand, very small quantities indeed of impurities such as benzal chloride, benzyl chloride and tarry substances, which occur in some commercial preparations, produce relatively severe damage.

Chakravorti[89,90] has shown that exposure of paper to 'gammexane' smokes reduces both the tensile strength and the folding endurance. When used at the dosage recommended for disinfestation of stored products (2 oz./cu. ft.) the tensile strength and folding endurance were reduced by 53·7 and 71·5% respectively.

Such damage, which occurs even with the best rag-made papers, is of obvious importance when valuable and historical records are concerned; it is thought to be partly associated with the acidic decomposition products of the smoke-generating materials in the canisters.

Busvine and Kennedy[91] have observed that unless adequate precautions are taken both DDT and gammexane smokes are liable to taint foodstuffs exposed to them. Gammexane in particular was found to be absorbed on greasy surfaces, which subsequently emitted a characteristic musty odour for long periods. Although the method of smoke generation uses many times as much insecticide as spray-application methods it is cheap and easy to use, and fairly effective in reducing fly populations. Part of the reduction of fly populations, as well as that of cockroach populations, may be attributed to emigration from the treated quarters rather than actual extermination of the insects. Some interesting observations were made on the physical state of the deposited insecticides, comparable with those of Block reviewed in the last report. The large dendritic aggregates of BHC crystals on cobwebs are particularly noteworthy.

Benzene hexachloride has been shown[92] to be a more dangerous poison to bees than DDT. This conclusion is valid not only for honey-bees (*Apis mellifera*) but also for the long-tongued wild bees belonging to the various species of *Bombus* and *Psithyrus*. These genera are particularly important in areas where red-clover pastures are of economic importance, since this plant has too long a flower to be reached by ordinary strains of honey-bees unless the flower has been previously punctured by a parasite.

So far as sprays on open blossom in orchards are concerned, DDT preparations proved essentially safe both to honey-bees and *Bombus* spp. whereas benzene hexachloride remained dangerously toxic for at least three days after spraying. Part of the difference in toxicity has been ascribed to a repellency, associated with the carrier material, similar to that noticed elsewhere for DDT sprays. Lead arsenate was a little less toxic than DDT. Apart from any effect of the carrier, DDT sprays and dusts proved markedly repellent to the solitary bee *Andrena flavipes*, though not to honey-bees.

There is some experimental evidence that the contamination of pollen by DDT sprays is not likely to be of importance, as such contaminated food does not seem to affect the larvae unless the concentration of insecticide is very high, when the workers are killed before feeding the larvae.

Although the use of DDT on nectar-producing plants may lead, at first, to some reduction in bee population in the neighbourhood, the reduction may be followed by a rise in population and in activity occasioned by the improvement in plant growth brought about by successful pest control. Changes of this kind were observed with test hives in fields of lucerne dusted with DDT to control *Lygus*. Bees were marked with titanium oxide and basic fuchsin and a fall in field population and hive weight was recorded immediately after dusting; however, both recovered within a few days and were later succeeded by a rise, reflecting the increase in flow of nectar caused by *Lygus* control. It appears that, initially, the bees are repelled and not actually killed.[93]

The danger of ill-timed application of the more stable insecticides leading to severe increase in pests owing to the destruction of predators continues to be pointed out, particularly by Massee.

Although tainting of certain fruits, particularly with benzene hexachloride, is sometimes difficult to avoid, in some cases the rate of application and interval between spraying and harvesting may be so chosen as to avoid taint; cf. Snapp, on the effect of benzene hexachloride on peaches.[94]

Some quantitative observations have been made by Woodrow on the toxicity of DDT to bees.[177] Many bees are killed by as little as 6 μg. of DDT when they are fed individually with syrup containing the insecticide; considerable mortality results from the collective feeding of bees with syrup in which the DDT concentration is 0·1%.

Decomposition of DDT *in vivo* and *in vitro*

The causes of the toxicity of DDT to warm-blooded animals remain obscure in spite of extensive investigations.

Judah[95] has established that DDT in mammalian tissue does not liberate hydrochloric acid so that, whatever the cause of its toxicity to insects may be, dehydrochlorination is not responsible for toxicity to mammals. Dehydrochlorination would lead to the formation of the dichloroethylene derivative of DDT; but Judah finds that DDA (2 : 2-bis-*p*-chlorophenylacetic acid) is the only metabolite excreted from mammals and since the quantity of this metabolite is very low DDT must remain in the body for some time unchanged, possibly by storage of the insecticide in fatty tissue. DDA is, however, not of itself appreciably toxic and in view of its low concentration we must look elsewhere for the cause of the symptoms of acute poisoning. When DDT is administered blood sugar rises and then falls, but this effect is probably the result, rather than the cause, of the nervous convulsions typical of DDT poisoning.

The administration of calcium gluconate before DDT greatly reduced the symptoms, but the fact that DDT does not produce hypocalcaemia disposes of another possible theory, and adds one more unexplained fact to the main question: the unaccounted-for toxicity of DDT to mammals.

Dehydrochlorination does take place, however, when DDT is treated, even under mild conditions, with basic substances. Mono- and dimethylamine, trimethylamine and ammonia are active, decreasing in the order given, when the DDT is dissolved in benzene; dioxan, as a solvent, accelerates the decomposition.[96]

A study of the reaction rates in various solvents indicates the formation of a complex with the amine dimer, but attempts to isolate or prepare such complexes were unsuccessful. DDT in any single-phase system shows appreciable decomposition at p_H 7·1, the rate of reaction increasing up to p_H 11. Under certain circumstances this reaction is catalysed by Fe^{++}, Fe^{+++}, Cu^{++}, Al^{+++}, and Mn^{++} ions.

Hoffmann and Sendle point out that DDT is toxic to most invertebrates except for a few species of snails, annelids and crustacea[174] and that, on a weight basis, the insecticide is only slightly less toxic to warm-blooded animals. Working with isolated organs, no difference was found in the effect of DDT on smooth and striated muscle, and negative results were obtained when attempts were made to inhibit various enzyme systems. The latter point has been independently verified for cholinesterase systems in crushed suspensions of flies and Colorado beetles.[175]

Carter and Schechter[97] in an investigation of the fate of chlorinated hydrocarbon insecticides fed to cattle, have demonstrated that DDT, BHC and Toxaphene are all secreted unchanged in the fatty tissues, and also in the butterfat of the milk. The concentration of DDT, for example, was determined by the Schechter–Haller colorimetric reaction, and the residues from the biological material thus analysed were compared with the same concentration of pure *p-p'*-DDT in a biological assay. No discrepancy between the two preparations was found. It is not unlikely that the concentration of the chlorinated hydrocarbon insecticides in the milk and in certain organs of the body lessens the risk of meat becoming tainted from the spraying of animals. This may have a bearing on the absence of taint in pig-meat, established by Lehner *et al.* when the pigs were sprayed with benzene hexachloride only two weeks before being slaughtered.[185]

Reinschneider[98] has compared the acute toxicity to rats of several chlorinated- and fluorinated-hydrocarbon insecticides and of E605. Of these M410 (octachloro*endo*methylenetetrahydrindene), M414 (octachloro-*endo*methylenetrichloro*cyclo*hexane), DDT, *p.p'*.-difluorodiphenyltrichloroethane and benzene hexachloride are of the same order of toxicity. DDD is less toxic and E.605 more toxic. In chronic poisoning by M410 and by DDT, only when the food was contaminated to the extent of 0·4 g./kg. was there significant accumulation in tissues rich in lipoid such as the testicles, suparenals, thyroid etc., after one year. A warning of the necessity of exercising caution in toxicological work with insecticides and of care in the handling of new and potentially poisonous insecticides or acaricides is furnished by the death of Velhinger from chronic poisoning contracted during experiments on the evaluation of the acute toxicity of DDT and benzene hexachloride.[178]

The damage to plants produced by insecticides varies not only with the active principle but also with the solvent, emulsifying-, wetting- and spreading-agents and with the degree of dispersion or particle size of the spray or aerosol. A recent example is furnished by the work of Smith *et al.*[179] which deals with the effect of aerosols of DDT, hexaethyltetraphosphate, and 'parathion' (*o-p*-nitrophenyl-*O-O*-diethyl thiophosphate) on a large variety of greenhouse plants. DDT injured only kalanchoe and cucumber out of 150 different species and the damage to cucumber was

prevented by substituting a methylated naphthalene for *cyclo*hexanone as a solvent. Hexaethyl tetraphosphate damaged tomatoes and 30 out of 140 varieties of chrysanthemum, whereas parathion damaged only one out of 99 varieties of chrysanthemums and did not damage tomato or 40 other commercial greenhouse plants.

The effect of particle size of aerosols on their efficacy and on their phytotoxicity has been investigated by Fulton *et al.*[180] Under their conditions efficacy increased and damage decreased as the particle size was progressively reduced. The active principle used was hexaethyl tetraphosphate and the propellant was methyl chloride. The particle size was reduced either by increasing the proportion of methyl chloride or by increasing the pressure in the container, either by raising the temperature or by admixing carbon dioxide.

Apart from direct and obvious effects on plants, insecticides may produce indirect or masked effects such as an alteration in growth caused by soil fungicidal or bactericidal action or an alteration in rate of germination of seeds etc. According to Smith and Wenzel, DDT has no action on soil bacteria or fungi whereas benzene hexachloride acts as a fungicide and an inhibitor of nitrifying bacteria.[181] The effect of these actions varies with the plant and in some cases leads to better growth on account of the enforced change-over to ammonia metabolism. Toxaphene is actually used as a food by both types of micro-organism. Chapman and Allen find that DDT in low doses often promotes growth but at higher doses inhibits it.[183] This observation may be connected with those of Pickett[182] on the increase in oxygen consumption of peach leaves sprayed with a spray liquid containing 0–2 lb. of 50% DDT per 100 gal. The increase is particularly noticeable with young leaves, with which a similar increase is also brought about by spraying with lead arsenate alone or with lead arsenate and zinc sulphate. Chapman and Allen also observed that when DDT was used as a seed dressing there was a retardation of germination but that subsequently the growth of plants from treated seed caught up with that of the controls.

Wolfenbarger records an improvement in yields of potatoes sprayed with phosphatic insecticides, either alone or mixed with DDT, which is not accounted for solely by the control of aphides or other pests. Six applications per season of hexaethyl tetraphosphate (1–2 pints of 50% insecticide per 100 gal. were made and, in the case of parathion, nine applications were made of a spray liquid containing 2 lb. per 100 gal.). The extra improvement in yield is ascribed to the utilization of phosphorus by the plants. None but the simplest insecticides come into commerce as pure chemicals, so there is always the possibility that on the one hand impurities may produce taint or other objectionable effects or, on the other, that they may increase insecticidal efficiency. Recently it has been claimed that certain impure preparations of DDT were more effective, in the field, than the pure compound although nothing of this kind is commonly observable in the laboratory. With benzene hexachloride there seems no doubt that the most effective insecticidal preparations are those containing the highest content of the γ-isomer and these preparations are also the least irritating and least liable to cause taint. Some modern preparations have only a slight odour although a 'biting' sensation

can be produced by an aerosol which may under some conditions be objected to. Reference has been made recently to a preparation by Pennsalt,[9] by the use of partition chromatography, of a material containing 97% of the γ-isomer and stated to be almost odourless and non-toxic to mammals.

Insecticide-resistant strains of insects

The literature on this subject increases rapidly but exhibits increasing evidence of confusion, probably on account of the number of ancillary topics involved in each case.

The difficulties of experimental work in this field and of biometrical observations on natural insect populations are mainly of a biological nature, but the implications of such work are of considerable moment to the insecticide manufacturer and even more so to those concerned in advisory work and in applying insecticides in the field.

In this type of investigation, involving problems of a chemical, physical, genetical, entomological, biometrical and statistical nature, attention to the principles of experimental design is of outstanding importance. It is not, perhaps, too much to say that the majority of papers on the subject of resistant strains are made less valuable on this account, mainly by failing to distinguish between resistance acquired as the result of selection effected by an insecticide and resistance produced by other factors.

For example, Ricci[99] has discussed the different resistances of cockroaches from areas treated with DDT compared with those from areas not so treated; whereas Hansens[100] has similarly observed that stable-flies (*Stomoxys*) from DDT-sprayed barns appear to be more resistant than those from unsprayed barns. On the other hand, some of the effects reported are of such a magnitude that they can scarcely be accounted for by the natural fluctuations in the tolerances of the populations.

Sacca[101] has found that some houseflies can tolerate surface applications of DDT at no less than 4 g./m.^{2} and Bettini[102] has found that these remarkable tolerances extend to DDT injected in olive oil solution and to surface deposits of 5·3 g./m.^{2}, but that 2 g./m.^{2} of octachlor was effective against these resistant flies.[103]

The resistance acquired by insects surviving sub-lethal doses of contact insecticides in the laboratory appears frequently to be common to other contact insecticides having not too dissimilar modes of action. A general perusal of the literature indicates that resistant strains of houseflies selected after contact with DDT are also resistant to other chlorinated hydrocarbons, but not to the phosphoryl-ester insecticides. The evidence for resistance to the pyrethrins as a secondary effect of this kind is so confused that no opinion can properly be expressed on it.

A direct building up of a strain resistant to the pyrethrins is stated by Beckley to be unknown[104] and is certainly not a common phenomenon. Such a strain has, however, been produced in the laboratory with grain weevils as the test insects, but it may be that this strain would be less likely to survive under warehouse conditions as selection for resistance is associated with a reduction of fertility.[105]

A remarkable example of a strain of grain weevils resistant in the normally susceptible egg-stage to mercury vapour has recently become

established, apparently as the result of breeding the cultures in an incubator contaminated by the breaking of a thermometer.[106] In less than two years the strain is 16,000 times as resistant as it was when first examined for tolerance to mercury vapour, and the slope of the regression of probit mortality on log (dose) is much flatter than previously.

Locust control.—During the past few years intensive investigations have been carried out on the control of locusts both in the field and laboratory, and large quantities of insecticides are used for this purpose.

The comprehensive laboratory-investigations by Kennedy *et al.* reviewed in the last Report have been followed by behaviour studies in Kenya. The bulletin dealing with this topic[107] shows that the widely held view that migrating insects travel in one direction persistently may require modification. A swarm of desert locusts (*Schistocerca gregaria*) was followed for 18 days, during which it did show a general northerly trend ; but the most noticeable feature of the course taken was its zigzag character.

An important development in the spraying of locust swarms is outlined in a further bulletin.[108] The customary method of applying insecticides from aircraft has been to eject the spray from aircraft flying so low that the wind effect was minimized. In the new method, developed by various workers at the Chemical Defence Research Station, Ministry of Supply, the aircraft flies at a height predetermined so that the wind is used to obtain the desired spray-pattern on the ground. With the use of this 'Porton' method of applying the spray, extensive experimental trials in Tanganyika have given excellent results against the red locust (*Nomadacnis septemfasciata*). When used at the low rate of 1 gal. per acre, a 20% oil solution of dinitro-*o*-cresol (DNOC) gave effectively complete control.[109]

The relative toxicities of most of the insecticides likely to be of use in locust control have been determined by direct application with a micropipette. E605 was by far the most promising, and the relative ineffectiveness of DDT against these insects was again demonstrated.[110]

Measurement of toxicity of stomach poisons

A great deal of attention has been paid over the past few years to the contact toxicity of such insecticides as DDT, BHC, DNOC and the pyrethrins. The publication of a detailed investigation of the action of various substances as stomach poisons is therefore particularly welcome. The selection and rearing of suitable insects,[111] the technique of the biological assay system and some of its properties[112] and the effects of foliage as a substrate for the insecticide[113] have all been described.

Among other results, the proportionality of the body-weight of fifth-instar *Phlogophera meticulosa* larvae to the median lethal dose of lead arsenate greatly simplifies interpretation of the data from this assay system.

Particle size retentivity and contact toxicity of insecticides

The influence of particle size and shape of DDT crystals on their contact toxicity has been further studied, and the difficulties met with in the

earlier investigations of McIntosh have been to a large extent solved. This author[114] employed various solvent-exchange methods to control the form and size of the crystals, ranging from the colloid produced by pouring a solution of DDT in alcohol into water to the needles, of length approximately 400 μ., formed by slowly adding acetone solutions of DDT to mixtures of sulphonated lorol and water.

The resulting suspensions were tested against *Tribolium castaneum* by a dipping technique and the results to a large extent verified by direct spraying of the insects in a Potter tower apparatus.

Contrary to expectation, it was found that the coarser suspensions were more toxic than the finer suspensions, and all were more toxic than the colloid. McIntosh was able to determine the weight of DDT retained by the dipped insects and found this quantity was also directly related to the particle size, so that on the basis of DDT retained by the insects the toxicity of the suspensions was substantially independent of the particle size. The colloidal preparation of DDT from alcohol was found by McIntosh to give a probit regression line of different slope from that common to all the other preparations, when the independent variate is the log (concentration) of DDT. Such a change of slope is commonly held to indicate that the mode of action of the insecticide has in some way been altered, and the interpretation of the phenomenon in this manner would be difficult.

The plotting of the data in the manner outlined above implies that the weight of insecticide received by the insects is directly proportional to the concentration of DDT in the suspensions. Stringer[115] has repeated and extended that part of McIntosh's work which relates to the colloidal preparation of DDT and some of the suspensions of needles and finds that the direct proportionality between applied and received doses, as used by McIntosh, is not the appropriate relationship for this assay system.

Stringer points out that only a relationship of the type $W = k\lambda$ where W is the weight of DDT retained on the insects, λ the concentration of DDT in the suspensions, and k and f are constants, will satisfactorily account for the differences of slope in the probit–log (concentration) regression lines for the colloidal and needle shaped suspensions. With such a relationship, a change of slope corresponds to a change in f in the equation. The constant f is termed an 'availability constant' and it is shown that a relationship of the type given above fits the data more satisfactorily than the direct-proportionality hypothesis of McIntosh, expressed by $W = k\lambda$. The availability coefficient was also found to be proportional to the slope of the regression line, so that it should prove a useful and readily estimated parameter for difficult biological assay systems.

Dry deposits of DDT were found to be unsuitable for biological assay against *Calandra granaria* since the slope of the regression line was so slight that the assay was too insensitive. Assay of DDT by spreading oil-films containing it over filter papers was satisfactory, but only if the volume of oil applied was kept constant and the concentration of insecticide varied. A variable thickness of oil film introduced curvature into the probit regression lines owing to the action of the oil, even at low doses where the oil by itself would not exert any effect on the insects.

McIntosh[116] has recently found that DDT crystals of short length are less toxic at equal surface dosages at high temperatures than are those of greater length, whereas the converse is true at lower temperatures.

On the other hand, Fan *et al.*[117] have found that DDT has a negative temperature-coefficient of mortality as a function of dose at low temperatures whereas at high temperatures the converse is true. These experiments were carried out on mosquito and midge larvae in water; by injecting crane-fly larvae a positive temperature-coefficient was obtained at all the dosage levels tried.

Physico-chemical factors in biological assays

In the system involving DDT suspensions that has just been discussed, the amount of DDT retained by the insects can be estimated by the convenient colorimetric method of Schechter *et al.*[118] When other and less easily detected insecticides are used special devices must be adopted to investigate the important relationship between applied and received dosage. Much work of chemical interest on the toxicity of insecticides and fungicides depends on the correct interpretation of biological assay data, and it is becoming increasingly clear that the almost universal assumption of proportionality in the relationship given above is sometimes unjustified; this invalidates the interpretation of the data. The failure to examine the assumption when unusual dosage–response relationships are obtained is the more dangerous because the assumption is usually made tacitly.

The quantity of pyrethrins accumulated by *Aedes aegypti* mosquitoes flying through sprayed pyrethrum emulsions has been determined.[119] Since the pyrethrins cannot be determined in very small quantities aluminium chloride was incorporated in the water-base sprays used and the metal was determined microcolorimetrically after low-temperature incineration of the insects. In this assay system also, the relationship between the concentration of the pyrethrins in the spray and that acquired by the insects is complicated but the responses of the insects occur when they have acquired a constant weight of the insecticide. Stimulation to flight occurs when $1{\cdot}20 \times 10^{-7}$ mg. pyrethrins has been accumulated and paralysis sets in when $6{\cdot}0 \times 10^{-7}$ mg. is picked up.

From the limiting time of the diffusion of the insecticide through the insect cuticle it is possible to determine the thickness of the barrier between the site of action and that of application. The figure arrived at, approximately $0{\cdot}4\ \mu$., agrees well with that of Beament[120] for the thickness of the waxy epicuticle.

The physico-chemical factors influencing the penetration of insecticides through the cuticles of insects has been discussed by Hurst in terms of the behaviour of the cuticle as an asymmetrical membrane.[121] Hurst does not follow Beament in his suggestion that there is a continuous waxy epicuticular layer on the chitinous cuticle. This suggestion, and a general discussion of the nature of the chitinous part of the cuticle, has been developed in a general survey by Wigglesworth.[122]

Hurst concludes that the fatty material is present in the form of discrete lamellae parallel to the cuticular surface and orientated with the chains at right angles to the cuticle surface. This author suggests that, on

the evidence of four bright diffuse spots of the 4·15-A. ring of the X-ray diffraction patterns of the cuticle surface, the unit cells of the fatty components of the cuticle are analogous to the orthorhombic unit cells of n-paraffins and fatty acids (cf. Cowley[123]). It is also considered that these unit cells are probably associated in layers between the structural protein fibrils of the cuticle, with the dimensions of the cells corresponding to the distance between three side chains on a protein chain in the β-keratin configuration (7 A.) and the inter-chain distance (about 5 A.).

There would appear to be a difference of opinion between the views of Hurst[121] and Wigglesworth[124] on the mode of action of inert dust insecticides. Wigglesworth's view was that the dusts abraded the epicuticular layer (continuous) of waxy materials, and this allowed water to escape from the surface of the insect. On the other hand, Hurst considers that the water-control mechanism of the insects are the lipoid cells previously mentioned in their association with the proteins present in the cuticle. The network of lipoid cells, functioning as a valve, is considered to be 'opened' and 'shut' by deficiency or excess of free (unbound) lipoid material. Water vapour has been shown to escape through waxy molecular films only when the surface pressure is below a certain critical level. In contact with an excess of waxy material, the compression of many films renders them relatively impermeable to water vapour. As Hurst indicates, the essential point is the mechanism of the 'valve' action, which he believes to be the hydration of the polar interfaces between the lipoid and protein structural units of the cuticle. In damp air liquid water is condensed at these interfaces, thus expanding the mosaic of protein and lipoid. In dry air this liquid water is evaporated causing compression of the cuticular valves, and preventing transport of water vapour across the cuticle from inside to outside. On the other hand, if an insect in need of water is placed in a damp atmosphere the valves act as 'pumps' so that water is condensed at the interface and forced into the body fluids.[125]

These different interpretations of the cuticular structure of insects lead immediately to the corresponding differing views on the mode of action of the inert dust insecticides. The original hypothesis that certain inert dusts, such as powdered alumina, exerted a desiccating action on insects by abrading the continuous waxy epicuticular layer, and the abrasion permitting the passage of water vapour, was given by Wigglesworth.

The superficial abrasion is demonstrated by staining with ammoniacal silver hydroxide solution, a deposit of silver being formed by reduction with the polyphenols present in the proteinacious part of the cuticle. As Hurst[121] points out, however, the abraded insects do not lose moisture when removed and washed from damp alumina, so that a possible alternative mechanism for the desiccating action lies in the capacity of the dust to adsorb and fix the mobile lipoids in the cuticle ; this prevents the insects from closing the valve mechanism mentioned above to reduce the passage of water vapour.

The retention of insecticidal suspensions and powders by insects is paralleled by their retention of insecticides applied to surfaces as films. Musgrave[126] suggests that the presence of traces of organic solvents

account for the greater toxicity of films of 'technical'-grade benzene hexachloride when compared with 'refined' samples of this material. This suggestion has been carried further by Deffner and Augustides[127] who attribute the greater toxicity of such films to their greater retention by the insects. These authors used both benzene hexachloride and phenyl *iso*nitrile, and found that the toxicity was independent of the organic solvent used. Deffner and Augustides observe that phenyl *iso*nitrile is repellent to *Eurytoma pistaciae* and *Idiocerus pistaciae*. Muirhead-Thomson,[128] however, has suggested that the repellency of DDT as normally applied to native huts in kerosene is a more complicated phenomenon than was at one time thought. It has been shown that the marked initial repellency to *Anopheles gambiae* mosquitoes of such applications was due primarily to the kerosene.

Under comparable conditions benzene hexachloride does not produce the same irritation in alighting mosquitoes as DDT, with the result that the insects remain in contact with the insecticide long enough to accumulate a lethal dose. The protection afforded by benzene hexachloride is thus superior to that of DDT and it lasts for about three months. From other sources, too, comes the evidence for the relative ineffectiveness of DDT residual treatment as an antimalarial measure.[129]

Relationship of toxicity to chemical structures

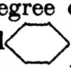
This subject, of perennial interest, has stimulated a further series of papers subsequent to those reviewed in last year's Report.[130] The drift of current opinion is clearly towards the view that although for many insecticides toxicity may be associated with specifically reactive groups, certain general features of a physical nature, such as molecular volume, must be satisfied before the insecticide molecule can become effective at the site of action; this view was foreshadowed by Busvine.[131,132]

Lord[133] has examined a large series of compounds related to DDT for their relative potencies against the chrysanthemum aphid (*Macrosiphoniella sanborni*) and a grain beetle (*Oryzaephilus surinamensis*). Four of the isomers of hexachloro*cyclo*hexane were also investigated, of which only the γ-isomer was found to have a toxicity which compares with that of DDT. Of the others, the δ-isomer was the only one with measurable toxicity under the experimental conditions used. This paper was written before it became known that the γ-isomer does not have the i-inositol structure formerly assigned to it, so that the interpretation of the toxicities requires reconsideration.[130]

So far as the DDT analogues are concerned it was found that, in general, the relative potencies were large for those compounds having molecular weights lying between 200 and 450 and fell off abruptly on either side of this range. Much the same relationship holds when the relative potencies are plotted against the parachors. It is possible that this observation by Lord is connected with the fact that the pyrethrins and cinerins, and many of the most important synergists for these compounds, also have molecular weights within this range. Lord[135] also found that the DDT analogues behaved similarly so far as their sorption by chitin is concerned. The same author[133] did, however, observe that the slope of the probit regression lines was more closely related to molecular

weight. This observation may be of importance when the slope of the regression line is interpreted in terms of the 'availability coefficient' of Stringer,[115] since by this means it should be possible to sort out the effects of molecular structure on the passage of the substance to the site of action in the insect, as opposed to the toxic effect at that point.

Lord[134] has further examined the effect of the insecticides mentioned above, and some others, on the respiration rates of the grain beetle previously used. It was found that DDT and its analogues, hexachloro-*cyclo*hexane, 3 : 5-dinitro-*o*-cresol, and the pyrethrins, formed a group of substances which first stimulated the insects to increased respiration, and then slowed down this response. Lethane B71 and rotenone do not give rise to any primary stimulation. In addition, the rate of respiration and length of life of insects treated with DDT dusts were independent of the DDT concentration provided that a lethal dose could be accumulated by the insects. So also were the total volumes of oxygen consumed, which were indeed the same as those consumed by untreated insects : this led to the suggestion that the insects die when their energy reserves, or some similar factor, become depleted. The hypotheses for the mode of action of DDT have been reviewed by Stringer,[136] who points out that although the site of action has been more or less established as the peripheral nervous system of the insects, the mode of action still remains obscure. The dehydrochlorination hypothesis, by which facile elimination of HCl was held to confer toxicity on insecticides whose other properties enable them to penetrate to a suitable site of action, has been rejected for certain new chlorinated-hydrocarbon insecticides.[137] A specific example was 'Compound 118' or 1 : 2 : 3 : 4 : 10 : 10*a*-hexachloro-1 : 4-5 : 8-di*endo*methano-1 : 4 : 4*a* : 5 : 8 : 8*a*-hexahydronaphthalene, which is stable to alcoholic potash. It is, however, pointed out that the differences in the rates of action and qualitative differences in the symptoms produced by 'Compound 118' when compared with compounds thought to act by dehydrochlorination indicate that the modes of action are dissimilar.

Kips and R. L. Wain[138] have investigated a large number of halogenated hydrocarbons and found no correlation between the ease of dehydrochlorination and insecticidal activity. On the other hand, it has been found[136] that DDT analogues with the groups $=CH{\cdot}CCl_3$ $=CH{\cdot}CH{\cdot}Cl_2$ and $=CH{\cdot}CH_2Cl$ are of increasing effectiveness as the degree of chlorination is increased. The comparatively toxic analogue Cl$\cdot CCl{:}CCl_2$ is compared with the ineffective ethylenic DDT derivatives. Dehydrochlorination in the first compound is impossible, and its toxicity relative to the ethylenic DDT analogues suggests that a major factor may be the special configuration of the molecule.

Compared on a molar basis, DDT and its *p*-bromo analogue are of approximately equal effectiveness, but the *p*-iodo derivative has only half this toxicity. Again on a molar basis, the toxicity of DNOC to grain weevils was not increased by incorporating in the hydroxyl group the phenyl mercury base.[139] In the same investigation, Velsicol 1068 (chlordane) and toxaphene (chlorinated camphene) were shown to be less toxic than DDT, and E.605 about 10 times as toxic as the same reference

insecticide. It may be useful to recall here that the quantitative estimates of the relative potencies of insecticides with differing modes of action are only a very rough guide to their performances. The term 'relative potency' has no clear definition when the slopes of the probit regression lines of the several compounds are unequal.

The insectical action of the chlorinated *p*-chloroethylbenzenes has also been examined[140] and the most active constituent of the insecticide formerly known as 'Lucex,' prepared by side-chain chlorination of 4-chloro-1-ethylbenzene, is most probably the $-C\cdot Cl_2\cdot CHCl_2$ derivative.[139] The $-CHCl_3$ group alone is not, however, a requisite for activity.[176]

Lepage *et al.*[141] have examined a number of DDT-like substances, and have obtained interesting results in tests against the locust *Schistocerca cancellata*. Some less usual substitutents for the $-CH\cdot C\cdot Cl_3$ grouping in DDT have been examined and it was found that the $=SO$ group lowered the toxicity, but that $\equiv PO$ and $\equiv PS$ increased it, the latter by a considerable factor.

Gersdorff[142] has given a review of the relationship of structure to toxicity in the pyrethrins and pyrethrinoid series, and has also demonstrated[143] that the synthetic allyl analogue of cinerin is about six times as toxic as the natural mixed esters, at least so far as houseflies are concerned.

Organo-phosphorus compounds

In the last Report reference was made to the chemical and insecticidal properties of tetraethyl pyrophosphate and its congeners, and also of E.605 (*p*-nitrophenyl diethyl thiophosphate). A conference on these and similar topics was held by the Association of Applied Biologists and much interesting progress was recorded.[144,145] H. Martin reported that E.605 has marked ovicidal properties, inhibiting the hatching of aphis and winter-moth eggs at 0·05% (w/v) or lower concentrations. It has been suggested[146] that E.605 is a true systemic insecticide, that is one which is absorbed and is translocated within the plants to which it is applied. The residues left in the plant would then require careful investigation before the plants could be used for human or animal consumption.

Several other compounds[147] can be translocated within plants, notably fluorobisdimethylaminophosphine oxide, $(NMe_2)_2PFO$, which is stable to water, and the tetrakisdimethylamide of pyrophosphoric acid, $(NMe_2)_2PO\cdot O\cdot PO(NMe_2)_2$. A further insecticide, bis-β-fluoroethoxymethane $CH_2(O\cdot CH_2\cdot CH_2\cdot F)_2$ is also systemically insecticidal, although it does not contain phosphorus. All these compounds, when watered on the roots of plants, cause the leaves to become toxic both to warm-blooded animals and to insects.

A succinct review of the syntheses of most of the important organo-phosphorus derivatives has been given by Coates,[147] together with the available data on their hydrolysis reactions. Bennett[148] has shown that all the three systemic insecticides mentioned above are phytotoxic, some at very low concentrations; he points out that much of the present work on them is of fundamental interest but is not likely to give immediate practical results.

Sodium selenate, an older systemic insecticide, has been shown to inhibit the reproductive processes of grain weevils and eelworms at low concentrations by which the adults are otherwise unaffected. The three insecticides discussed by Bennett have all been shown to exert a marked fumigant action, though that from the tetrakisdimethylamide of pyrophosphic acid was very slight against some insects and negligible against others. It appears that when the three substances are applied to the soil in which plants are growing the initial action is a fumigant effect; the systemic effect sets in later.

A most unexpected factor emerged when the speed of translocation of these compounds was studied. Brassy Willow beetles (*Phyllodecta vitellinae*) were imprisoned on certain leaves by glass tubes, which were then sealed. Such leaves remained non-toxic to the beetles even when neighbouring leaves were rapidly lethal. Bennett suggests that the build-up of saturated water vapour inside the tubes either prevents passage of the insecticide into the leaf or else inhibits the vaporization of the compounds from the leaf surfaces. At open surfaces the toxicity of the insecticides by fumigant action was roughly 100 times as great as from aqueous solution. Both these sets of observations will doubtless stimulate further work.

Eaton,[144] in discussing these contributions, suggested that toxicity to *Aphis pomi* eggs is associated with the incorporation into the phosphoric or thiophosphoric acid residues of two alkyl groups and an aryl group. Toxicity was increased by introducing electron-attracting groups in the *para*-position of the aryl group.

A further general review of these compounds and their properties has been given by Martin,[149] and a timely reminder of their toxicity to warm-blooded animals has also appeared.[150]

Analysis

Organo-phosphorus compounds.—Relatively few methods have been described for the analysis of these substances. Tetraethyl pyrophosphate (TEPP) and its crude mixture, so-called hexaethyl tetraphosphate (HETP) may be determined by fractional distillation for purification of the active ingredient followed by hydrolysis to diethyl orthophosphoric acid, which may be estimated titrimetrically.

Only one method for the analysis of parathion has been described which is generally reliable.[152] The insecticide is dissolved with KCl and gelatin in a mixture of acetone and water, and the quantity of parathion present is determined by polarographic electrolysis.

A colorimetric method was offered by Averell and Norris,[153] which is said to depend on the reduction of the diethyl *p*-nitrophenyl thiophosphate to the corresponding *p*-amino-derivative, and diazotizing and coupling this substance with *N*-(1-naphthyl)-ethylenediamine. An intense magenta colour certainly results from this process, but it has more recently been shown that the commercial grades of benzene give an identical colour when used for stripping residues of parathion from leaves etc.[154]

Distillation of the stripping solvent helps to reduce the interference, and it has been shown that pure parathion can be prepared to act as a primary standard quite readily.[158]

Piperonyl butoxide.—Piperonyl butoxide, one of the most efficient of the pyrethrum synergists, occurs in so many pyrethrum formulations that methods for its analysis are becoming necessary.

This substance gives a blue colour on treatment with tannic acid mixed with phosphoric and acetic acids. Since the synergist is usually analysed in admixture with the pyrethrins, the obscuration of the colour by these compounds is a serious source of interference which can, however, be removed by saponification with alcoholic NaOH before the test is undertaken.[156]

Hexachlorocyclohexane (BHC).—Marrison[160] has described a method based on the infra-red spectrograph for the rapid analysis of the stereoisomers of BHC. Nitromethane as a solvent was found to satisfy the somewhat exacting conditions of this analysis, so far as the γ-isomer was concerned, but owing to the lower solubility of the α- and β- and δ-isomers in this solvent, methyl acetate was used for the analysis of these constituents.

Various impurities were discovered in the course of a large number of analyses of samples of BHC including *p*-dichlorobenzene, hepta- and octa-chloro*cyclo*hexanes, and also the ϵ-isomer of the hexachloro derivative. A chloro derivative of *n*-hexane was also isolated. The method was standardized so that 400 samples per week could be analysed with a precision of about 3%.

BHC may also be determined, though not yet in terms of its isomers, by dehydrohalogenation with alkali, followed by ultra-violet-absorption analysis of the 1 : 2 : 4 :-trichlorobenzene produced.[161]

Of less general utility in routine work, though valuable for special purposes, are the infra-red spectroscopic methods of Daasch,[162] and that of Trenner *et al.*[163] The former differs from Marrison's method in that the higher *cyclo*hexanechloro-derivatives interfere, and the latter requires the use of a tracer molecule of γ-hexadeuterohexachloro*cyclo*hexane. Impurities, however, do not interfere with this mass isotope dilution method. The infra-red spectrogram used by Daasch has recently been corrected.[164]

It is claimed for a method based on partition chromatography between nitromethane and *n*-hexane on silicic acid that the γ-isomer of BHC can be determined as a routine method of analysis, to an accuracy of some 2%. For relatively pure preparations of this isomer, a cryoscopic method in which the measurement of the lowering of the freezing point by impurities is measured is said to provide a simple and reliable method of determination.[166]

A modification of the total-chlorine method of determining chlorinated hydrocarbons by hydrolysis enables this rather unspecific method to be applied to mixtures of BHC and DDT.[167] Essentially, the DDT is determined colorimetrically by the Schechter–Haller method (*see* last Report) and the contribution of the determined quantity of DDT to the total chlorine calculated, that from the BHC following by difference.

For BHC preparations not containing other chlorinated insecticides, La Clair has developed a method of dehydrochlorination in which the different rates of reaction of the four common isomers are utilized. The α- and δ-isomers react with N-ethanolic KOH at 0° C. within 15 min., whereas the γ-isomer takes 50 minutes for complete reaction. The β-isomer does not dehydrochlorinate under the conditions used.[169]

Two physical methods of estimating the γ-isomer have been proposed, both based on the fact that this isomer is the only one reduced at a dropping mercury electrode.[170,171] This latter method has been further developed by the use of a recording Heyrowsky polarograph, using hydrogen as the agitating gas rather than nitrogen.[157]

Of possible laboratory interest is a micro-method of estimating total chlorine by fusion of organic compounds with potassium, followed by a silver nitrate titration. This method might prove valuable for the analysis of deposits on surfaces, e.g. of insects.[159]

DDT and related compounds.—The methods for the analysis of DDT based on the determination of all or part of the chlorine content have been very thoroughly investigated and numerous modifications for special purposes have been suggested. Similar intensive investigation has been accorded the colorimetric methods and both types of determination have recently been reviewed by Haller.[172]

Fairing[169] has given a colorimetric test for 'methoxychlor,' the di-(p-methoxy) analogue of DDT. The reaction product of methoxychlor with alcoholic KOH is extracted with ether and a cherry-red colour is developed on treating the evaporated ethereal residues with concentrated sulphuric acid. This reaction will detect some 5 μg. methyoxychlor. Other compounds have not been found to interfere.

Since nitration plays an important part in the colorimetric estimation of many chlorinated hydrocarbons, the characterization of the nitration product of methoxychlor is of interest, the product being 1 : 1 : 1-trichloro-2 : 2-bis-(3-nitro-4-methoxyphenyl)-ethane.[173]

Acaricides

The differential susceptibility of mites and many insect pests has long been known and although it often necessitates special treatment to secure control of both mites and insects, advantage can be taken of it to free insect cultures from mites which are attacking them. A study of the susceptibility of mites to a well known insecticide and to compounds related to it is, therefore, of great practical and theoretical interest. Such a study has been made by Metcalf[187] based on DDT and the citrus red mite, *Paratetranychus citri*, and for insecticidal activity the greenhouse thrips, *Heliothrips haemorrhoidalis*, the mites and thrips being exposed to residues of DDT on Valencia oranges. In conformity with experience in the field, DDT showed negligible acaricidal activity as did all the related trichloroethanes, some of which, however, were of considerable insecticidal value. Changes in the aromatic substituents in DDT produced always a marked decrease in insectical without any appearance of appreciable acaricidal activity. Changes in the aliphatic part of the molecule,

however, while decreasing insecticidal action led to the appearance of appreciable acaricidal action, 2 : 2 : bis-*p*-chlorophenyl-1 : 1 :1-trifluoroethane being considerably acaricidal and bis-*p*-chlorophenylmethane even more so. Replacement of the trichloromethyl group by groups containing oxygen caused only a slight increase in acaricidal activity measured by the effect on *P. citri*, but one such compound, 1 : 1-bis-*p*-chlorophenylethanol was very effective against *Tetranychus bimaculatus*.

Other notable acaricides were *p*-chlorobenzyl *p*-chlorophenyl ether and bis-*p*-chlorophenoxymethane, the latter compound being almost inactive, however, against *T. bimaculatus*. Changes in the substituents in the rings of these compounds led to decreased activity. Of a series of compounds containing a single *p*-chlorophenyl group only one, 2-(*p*-chlorophenyl)-1 : 1 : 2-trichloroethane -1-ol showed appreciable insecticidal or acaricidal activity. In the author's opinion the behaviour of many of the compounds studied cannot easily be reconciled either with the theory of Lauger or with that of Martin and Wain on the mode of action of DDT and of related compounds.

In the year following Metcalf's publication a description has been given[187] of a pilot plant for the production of 1 : 1-bis-*p*-chlorophenylethanol under the trade names of 'Dimite' and DMC. The process involves the use of the Friedel–Crafts and Grignard reactions on a manufacturing scale. It is interesting to recall Metcalf's finding of the specificity of this compound. The acaricidal activity of 2 : 2-bis-*p*-chlorophenyl-1 : 1 : 1-trifluoroethane noted by Metcalf recalls the claims made by Riemschneider[188] for the insecticidal action of the fluorine analogue of DDT, 2 : 2-bis-*p*-fluorophenyl-1 : 1 : 1-trifluoroethane and the compound with fluorine instead of chlorine only in the rings : 2 : 2-bis-*p*-fluorophenyl-1 : 1 : 1-trichloroethane. The latter was stated to be ten times as effective as DDT and to be harmless to man. Probably neither part of the statement can be taken at its face value but they do suggest that some such compound having high insecticidal and acaricidal properties may be found.

Eggs of certain mites are susceptible both to petroleum oil sprays and to various dinitrophenolic compounds. It seems that the variable results obtained in practical control may be largely caused by the increase in susceptibility which sets in as the egg develops. Chapman and Pearce[189] in studying the control of the European red mite found, for example, that a 0·25% petroleum oil spray, applied when mites were about to emerge gave about the same degree of control as a 3·0% oil spray applied 39 days earlier. An effective dinitro compound against this mite was the triethanolamine salt of dinitro-*o*-*sec*.-butylphenol; dinitro-*o*-cresol was ineffective. Mixed ethyl phosphates added to DDD have been found to be effective in controlling the Willamette mite attacking raspberries; hexaethyl tetraphosphate is useful in controlling red spider on roses and leads to an increase in growth so striking as to suggest that there is some stimulatory effect on the plant.[191]

An account of the increase of red spider in certain warm districts in South Australia brought about by spraying with DDT to control codling moth is given by Kemp.[190] In irrigated areas the increased mite damage more than offset the reduced damage by codlin moth. White oil emulsions

gave moderate control of red spider,[189] whereas hexaethyl tetraphosphate proved superior to nicotine as an acaricide.

Fumigants

The volume of new work on fumigants is not large but accounts of work mentioned in last year's Report have now been published[198,199] and are available for consultation. The most interesting communications concern the fumigation of plant nematodes, particularly those in the soil, and fumigation in which, at some stage, the air pressure within the fumigation chamber is reduced—so-called 'vacuum' fumigation.

As regards eelworms which can be fumigated on true seeds or on seed potatoes and can therefore be treated in chambers, Goodey[200] has shown that the eelworm, *Anguilulina dipsaci*, is seed-borne in red clover and in teazle as well as in onion and can be controlled in all three by fumigation with methyl bromide at the same dose as that required with onion seed, viz. a concentration–time product of about 700 mg. hr./l. at normal storage temperatures if the seed is also dry enough for normal safe storage. The germination of treated seed appears to be, if anything, slightly better than that of the control seed, and there is a noticeable fungicidal action which results in 'cleaner' seedlings. Lubatti[201] has shown that commercial bags of seed are readily penetrated. The work needs extending to establish the relationships between dosage, water content of seed, temperature, sorption, susceptibility of the eelworm and susceptibility of the seed, as measured by germination, stand and yield.

Having regard to the established practicability, under certain conditions, of fumigating onion seed which is rich in sulphur compounds that are readily attacked by methyl bromide (*see* ANNUAL REPORTS, 1948), it seems likely that there are reasonable ranges of conditions under which teazle and red-clover seed can safely be fumigated. A chamber for the fumigation of red-clover seed, on a commercial scale, has already been constructed in this country. Bearing in mind the catalytic effect of mercury, derived from seed dressings, in promoting the reaction between methyl bromide and sulphur compounds and which, in onion seed, can lead to serious damage, it would seem advisable in the first place not to dress teazle or red-clover seed which is to be fumigated. It would be worth while to find out whether fumigation of seed with methyl bromide would in some instances render dressing unnecessary.

A study of the keeping qualities of seed potatoes fumigated with methyl bromide for the control of the root eelworm *Heterodera rostochiensis*, cysts of which adhere to seed lifted from infested ground, is being continued by Lubatti[202] and co-workers. Observations are also being made on the effect of fumigation on yield of three different varieties and on the combined effect of 'seed' dressing and fumigation. Results so far obtained appear to indicate that yield per tuber is not affected by fumigation and that good 'seed' which has not been dressed is usefully resistant to methyl bromide.

Three papers have been published by Peters on the eelworm, and soil treatment with DD or by heat,[203–205] one by Peters and Fenwick[206] on field trials with DD against potato-root eelworm, and two by Peters,[207,208] which deal with the problem from a more general point of view. The

effect of injecting DD into soil infested with *H. rostochiensis* and subsequently to be used for growing potatoes is complex on account of 'soil amendment' action. 'Soil amendment' is taken to consist of partial sterilization of certain soil micro-organisms and leads to an improvement in growth or increase in yield which may, in turn lead to an increase in the eelworm population. On these matters, Peters comes to the following conclusions from his pot experiments[208]: The height of plants at about the forty-fifth day after planting and the weight of all tubers produced are the two most useful criteria of growth and yield. In the first season the presence of numerous cysts does not affect growth or yield but plants grown in the same soil in the succeeding year are dwarfed and produce a much smaller crop. Injection of DD at 1460 lb. per acre increases the yield even in the absence of eelworms, the increase being about 28% of that produced by steam sterilization. In the second season there appears to be only an increase in height and yield resulting from a residual nematocidal effect. There is interference between the soil amendment effects of soil sterilization and of injection with DD. In heavily infected soil the benefit to be expected from application of artificial fertilizers is partly lost: the enhanced root growth is partly utilized in producing more eelworm cysts rather than more tubers.

Steam sterilization delays the hatching of cysts, possibly exerting an effect antagonistic to that of the root-diffusate stimulant, and thus allows the plant to make good growth in the vitally important early stages and, by soil amendment, stimulates the formation of a good root system. Thus good growth and yield accompanied by an increase in the eelworm population to its optimum value may be expected. Somewhat similar results should result from DD treatment unless a high enough kill of eelworms can be secured. DD also exerts, initially, a phytocidal effect which retards growth, later to be countered by the soil amendment effect which stimulates growth. Large numbers of eelworms can be killed by DD but nothing is known of the rate of development of the survivors who continue to live in sub-lethal concentrations. If it is impracticable to secure a really high kill of eelworm it may be better to fumigate the soil after a potato crop and before a non-susceptible crop. This sacrifices the soil amendment effect on potato yield but avoids rapid build-up of population from surviving eelworms.

The paper by Peters and Fenwick[206] describes an important series of trials of the fumigation with DD of seven 2-acre sites on sands, silts and blackland soils infested with *H. rostochiensis*. Injections were carried out in the autumn and potatoes grown in the following year. Factors investigated were dosage 0, 200, 400 and 800-lb. per acre, depth of injection (4 or 8 in.) and the effect of rolling after injection. At the site where the most regular results were obtained there were increases in yield, kill of eelworms and in the eelworm population after the crop was lifted which were roughly proportional to the dosage. Under favourable circumstances it appears from these experiments that a 50% increase in yield and about a 50% reduction in eelworms 4 weeks after injection can be expected from 800-lb. per acre, but the subsequent growth of the eelworm population, accelerated by the larger root systems resulting from the soil amendment and initial eelworm kill, raises it above the population in

control plots at lifting time. The blackland soils gave a lower kill and a much smaller increase in yield as a result of fumigation than silts and sands. After injection in autumn the nematocidal and probably also the phytocidal effects of DD persist in the soil for many weeks. The increase of the population from the low value reached 4 weeks after injection to the high value after lifting is most striking. Whereas, in one instance, the multiplying factor for the control plots was 1¼, the factor for the treated plots, treated at 800-lb. per acre, was 5¾. The factor cannot continue indefinitely to increase proportionately with the dosage. At some higher dosage the factor would be expected to remain stationary and at higher doses still to decrease below that for the controls, but how bad the phytocidal effects would be and at what dosages these changes would occur cannot be guessed at in view of the complication of the biological system and our ignorance of the behaviour of the fumigant in the soil. The authors point out that according to Chitwood and Feldmesser[209] the mortality of hatched larvae in the soil is normally of the order of 90% on account of lack of available space on the roots. Unless more than this proportion are killed by the fumigant, the eventual increase recorded by Peters and Fenwick and caused by the increased root system available would be expected.

These trials were based on small-scale field experiments giving highly promising results which, however, have not yet been published. It is perhaps possible that the complex nature of the fumigant may account for some of the discrepancy between the two sets of trials. DD is stated to be a by-product in the manufacture of allyl plastics and to be 'a black, volatile liquid containing mainly 1 : 3-dichloropropylene and 1 : 2-dichloropropane, the former being considered the principal agent toxic to eelworms.' Such a product might well be expected to vary from batch to batch and, indeed, according to Fenwick[210] different samples have been shown to have different potencies against eelworms. In addition to possible synergism between components in such a mixture, the different concentrations of such components and their rates of travel and dissipation by sorption, chemical action, evaporation etc., in different soils would seem likely to lead to very variable results.

Differences in the results at the various sites serve mainly, in the reporters' opinion, to give prominence to the difficulty of developing soil fumigation without some knowledge of the behaviour of fumigants in soils of different chemical and physical composition, of different water contents and subject to different meteorological conditions.

The authors consider that the 'failure' of DD mixture in England, compared with its success in Long Island, is probably mainly explicable in terms of climate. Long Island is south of the latitude of Rome and also has a continental type of climate.

Results of field investigations into the efficacy of DD for controlling the eelworm *Heterodera marioni* are given by Heeley.[211]

McClellan *et al.*[212] have investigated the effect of soil moisture on the efficacy of 4 fumigants; chloropicrin, DD, methyl bromide and dibromoethylene against the eelworm *H. marioni*, and the fungi *Fusarium oxysporum*, *F. callistephi* and *Sclerotium rolfsii*. Cultures of the organisms were inserted 7 in. from the points of injection. All the fumigants are

stated to be more effective and to be retained longer in wet than in dry soil and at high rather than low temperatures. As regards the temperature effect, chloropicrin was most effective against the eelworm at 36·6° c. but had little effect at lower temperatures. DD was effective in 24 hrs at 36·6° c., in 3 days at 22·2° c. and had very little effect in 13 days at 12·6° c. This certainly provides a basis for Peters and Fenwick's suggestion for the failure of DD in England compared with the results achieved with it in Long Island. Against the fungi, methyl bromide had a considerable effect on *S. rolfsii* at 36·6° c. whilst dibromoethylene was effective against *S. rolfsii* at temperatures above 22·2° c. in 6 days, although it had little action on *F. oxysporum*.

As regards the fumigation of stored products, an extreme example of 'layering' or uneven distribution of fumigant has been found by Call[213] in commercial fumigations of dried fruit with a mixture of ethylene oxide and carbon dioxide in chambers.

Because of the risk of explosion inherent in the use of ethylene oxide by itself, referred to in the following section, it is customary to follow the recommendations made in a publication of the Department of Scientific and Industrial Research,[214] and to distribute solid carbon dioxide near the top of the chamber before admitting the ethylene oxide. The solid carbon dioxide is broken into small lumps and spread out on wood-framed trays of hessian or other porous material or simply scattered over the goods.

It has now been shown that this procedure often results in extremely pronounced layering. The temperature between the bottom layer of boxes stacked on dunnage placed on the floor may fall as much as 9° c. whereas that between the top layer of boxes falls only 1°. A high concentration of carbon dioxide is built up near the ground by the descent of the cold dense gas and a displacement of air plus ethylene oxide occurs which leads to a low concentration of ethylene oxide at this level. In conformity with previous experience of practical fumigation, these concentration differences are substantially smoothed out after about eight hours, by which time the concentration of ethylene oxide has been greatly reduced by sorption. The layering effect appears not to extend higher than the third layer of boxes and not to occur if even a slight movement of air is ensured during the first hour of the fumigation. Experimentally, stirring was provided by swinging a wood and hessian 'punkah' by means of a wire working through a copper tube in the wall of the chamber; the 'punkah' was suspended in a central gangway. Under these conditions the temperature became substantially uniform within 1 hr., the carbon dioxide was evenly distributed in from 2–4 hrs. and after the first 15 minutes there was no serious layering and improvement in the distribution of ethylene oxide was even more marked. These changes were reflected in improved penetration into boxes of fruit. In an experiment without stirring the concentration multiplied by time products of ethylene oxide for top and bottom boxes respectively, were 16 and 55 mg. hr./l. and in a parallel experiment with stirring the concentration multiplied by time products were 48 and 65.

The use of ethylene oxide as a fumigant has in the past been accompanied at rare intervals by explosions. Burgoyne and Burden[192] consider

that such explosions are associated with the endothermic nature of the gas, and observe that cool flames can be initiated at quite moderate temperatures in mixtures of ethylene oxide and air under atmospheric pressures. The same authors[193] have studied the conditions under which the decomposition of ethylene oxide becomes explosive, and find that the ignition is of a thermal character. Chain reactions do not apparently play an important part in the processes preceding ignition. In practical fumigations atmospheric contamination by dust particles may occur, particularly in flour mills and stores and in warehouses and silos in which grain is handled; the effect of these particles on the explosion limits of inflammable gas–air mixtures has been shown to include broadening of the limits of composition and temperature within which explosive decomposition can be initiated.[194] Considerable attention has been paid to the construction of a 'flow method' of examining inflammability limits of gases, in which the fuel–air mixture is subjected to an igniting source at temperatures of storage spaces.[195]

This fumigant has also been known to explode in cylinders after varying but lengthy periods of storage. This phenomenon is due to polycondensation catalysed by hydrogen and hydroxyl ions and indeed acids and bases in general.[197]

It appears that this polycondensation could only be prevented by excluding the catalytic agents responsible since the introduction of neutral buffers which would help to suppress the polycondensation, would also initiate hydrolysis. The hydrolytic reaction has the same activation energy as the polycondensation.[196]

The dependence of sorption and damage produced by fumigation on the moisture content and on other conditions in the fumigation of stored food is now well recognized. It seems that much more work is required to elucidate similar problems arising in fumigations in the field. An example of work already started is that of Bartholomew, Sinclair and Lindgren[216] on sorption and damage produced by hydrogen cyanide in the fumigation of citrus trees. Some of the results are rather surprising, e.g. the greater sorption by dry than by wet fruit and possible explanations suggest themselves for others, e.g. the irrecoverable hydrogen cyanide retained by mature fruit which may be caused by cyanohydrin formation. The paper opens up an interesting and important line of research which could be pursued with advantage.

Phillips and Bodenstein[215] have made use of forced ventilation in a large cylindrical tank of 56,345 cu. ft. capacity for the fumigation of cotton seed in charges of 500 tons at a time, with methyl bromide.

The practice of fumigating bagged goods such as grain and groundnuts under sheets is extending. Lighter and more flexible sheets are being used and are made of multi-ply fabric and plastic or rubberized fabric. Piles must be reasonably accessible so that there is room to sheet them down properly and to ensure effective junctions of sheets and an effective seal with the floor, which should be sufficiently nearly impervious. Joints with the floor are made by providing a generous overlap of sheeting and weighting down with lengths of chain, bags of grain etc. Joints between sheets are often made by allowing sufficient overlap, folding the top sheet

back and rolling the two sheets together until the overlap is used up in the roll.

A better way of making all joints is spraying with a viscous solution of plastic which sets, largely by evaporation of solvent, as the spraying proceeds. By varying nozzle settings and air pressure and thus the proportion of air to plastic in the 'atomized' spray, holes can be sealed and deposits with different mechanical properties laid down. The spray does not normally adhere to ordinary building surfaces etc., but is caused to adhere by pre-treating such surfaces with a special rubber solution. One proprietary plastic used for this kind of work is called 'Cocoon protective strippable packaging.'

Sealing with sprayed plastic is applicable to the gas-proofing of storehouses, used occasionally for fumigating goods, railway box cars etc., and opens up new possibilities of the fumigation of goods in the course of normal handling without the cost and inconvenience of passing through fixed fumigation chambers. It is possible, too, that plastic sealing may be of use in preparing ships' holds for fumigation. One of the greatest sources of re-infestation of transhipped goods, especially such as cross the Equator, is the residual infestation in ships' holds. Quick turn-round at terminal ports militates against effective treatment of the holds after unloading cargo, but if holds are fumigated when filled with cargo the fumigation may, perhaps, take place during the voyage.

Obviously the risks involved must be carefully assessed and a satisfactory technique developed.

If an effective and highly penetrating fumigant such as methyl bromide could be used, then great tonnages of goods might be dealt with and, as the period of exposure would be long, the concentration to be maintained would be low.

In many trades and for many commodities, fixed fumigation chambers will always be necessary and perhaps, in some instances, it will be advantageous for such chambers to permit of the employment of one of the so-called 'vacuum' techniques. Recently Lepigre[217] has published a book describing his investigations into the efficacy of such techniques and his reasons for preferring the one in which a mixture of air and fumigant is admitted, from a gas holder, to the evacuated chamber until the pressure is restored substantially to atmospheric. Lepigre deals at great length with engineering details and shows diagrams and photographs of plants of all sizes from small mobile units to very large complicated lay-outs. Lepigre's observations are confined to the effects of the treatments on test insects inserted into the goods before fumigation. Work is now in progress at two institutions in this country which should throw more light on the efficacy of this and other techniques. This work includes the chemical determination of penetration, sorption, etc. and the effect of reduced air pressure on the susceptibility of certain insects.

References

[1] Admin. Report, Dir. Agric., Ceylon, 1947 (4), 17

[2] Chittenden and Coomber, *Bull. imp. Inst., Lond.*, 1949, **46**, 230

[3] *Pyrethrum Post*, 1949, **1**, 20

[4] Hopkins, *E. Afr. agric. J.*, 1949, **14**, 36

[5] Croome, ibid., 146
[6] *Pyrethrum Post*, 1949, **1**, 2
[7] Ibid., 16
[8] *Chem. Tr. J.*, 1948, **123**, 536
[9] *Agric. Chem.*, 1949, **4**, 75
[10] Hendricks, *Parasitica*, 1948, **4**, 189
[11] *Chem. Engng. News*, 1949, **27**, 1058
[12] *Agric. Chem.*, 1949, **4**, 78
[13] *Chem. Tr. J.*, 1949, **125**, 76
[14] *Mfg. Chem.*, 1949, **20**, 393
[15] *Agric. Chem.*, 1949, **4**, 63
[16] *Chem. Agr.*, 1949, **61**, 400
[17] *Pyrethrum Post*, 1949, **1**, 9
[18] Ibid., 10
[19] Harper, S. H., ANNUAL REPORTS, 1948, **33**, 162
[20] *Roy. Aust. chem. Inst. J. Proc.*, 1949, **16**, 255
[21] *J. chem. Soc.*, **1946**, 463
[22] Ibid., 892
[23] *J. Amer. chem. Soc.*, 1948, **70**, 3707
[24] La Forge and Soloway, ibid., 2074
[25] La Forge, Schechter and Green, U.S.Pat. Appl., 1949
[26] Harper, S. H., *Chem. & Ind.*, **1949**, 636
[27] Dauben and Wenkert, *J. Amer. chem. Soc.*, 1947, **69**, 2074
[28] Crombie *et al.*, *Nature*, 1948, **162**, 222
[29] La Forge and Soloway, *J. Amer. chem. Soc.*, 1947, **69**, 2932
[30] Schechter *et al.*, ibid., 1949, **71**, 1517
[31] Idem, ibid., in press
[32] *Chim. et Industr.*, 1948, **30**, 165
[33] Gillam, A. E. and West, T. F., *J. Soc. chem. Ind.*, 1944, **62**, 23
[34] Beckley, *Pyrethrum Post*, 1949, **1**, 5
[35] 'The Analysis of Pyrethrum Flowers' (Imperial Institute, 1948)
[36] Mitchell, W., *Pyrethrum Post*, 1949, **1**, 7
[37] Mitchell, W. *et al.*, *Analyst*, 1948, **73**, 484
[38] Chen and Yuan, *Ent. News (Nanking)*, 1948, **44**, 44 (through *Bibliog. Agric. U.S. Dept. Agric.*, 1949, **13**, 92, Item No. 45925)
[39] Parkin, *Pyrethrum Post*, 1949, **1**, 16
[40] Blackith, R. E., *Ann. appl. Biol.*, 1950, **37**, in press
[41] Page, A. B. P., *et al.*, ibid., 1949, **36**, 225
[42] Page, A. B. P. and Blackith, R. E., ibid., 1949, **36**, 241
[43] Blackith, R. E. *et al.*, in preparation
[44] Bray, G. T. *et al.*, *J. Soc. chem. Ind.*, 1947, **66**, 275
[45] Graham, *J. Ass. off. agric. Chem., Wash.*, 1949, **32**, 372
[46] *Kew Bulletin*, 1948, **3**, 329
[47] *J. roy. Hort. Soc.*, 1949, **74**, 7
[48] *Mfg. Chem.*, 1949, **20**, 394
[49] Kuna and Heal, *J. Pharmacol.*, 1948, **93**, 407
[50] Graham, *J. econ. Entom.*, 1948, **41**, 217
[51] Ibid., 513
[52] *J. Amer. chem. Soc.*, 1949, **71**, 366
[53] *J. chem. Soc.*, **1930**, 6
[54] Raphael and Sondheimer, *Nature*, 1949, **164**, 707
[55] 116th Meeting, American Chem. Soc., Sep. 1949
[56] Crombie and Harper, S. H., *Nature*, 1949, **164**, 1054
[57] *J. chem. Soc.*, **1950**, in press
[58] *J. Amer. chem. Soc.*, 1948, **70**, 4234
[59] Ibid., 3086
[60] *Agric. Chem.*, 1949, **4**, 37
[61] Richards *et al.*, *J. chem. Soc.*, **1948**, 1610
[62] Holland *et al.*, ibid., 1672
[63] Jones *et al.*, *J. agric. Res.*, 1949, **78**, 191
[64] Pagan and Loustalot, ibid., 197
[65] *Analyt. Chem.*, 1949, **21**, 530

[66] *J. Ass. off. agric. Chem., Wash.*, 1949, **32**, 392
[67] Pagan *et al.*, *J. agric. Res.*, 1949, **78**, 413
[68] Reingardt and Zabudko-Reingardt., *Med. Parasitol (Moscow)*, 1945, **14**, 92
[69] *Trans. Molotov. Univ. Rostov-on-Don.*, 1946, No. 5
[70] *Jacobs Chron. Nat.*, 1949, **105**, 122
[71] Lindquist *et al.*, U.S. Dept., Agric. Bur. Entom. and Plant Quar. Bull. No. E-775, 1949
[72] Simanton, U.S.P. 2,463,324
[73] Blackith, R. E., forthcoming publication
[74] Page, A. B. P., and Blackith, R. E., *Ann. appl. Biol.*, 1949, **36**, 244
[75] Ranganathan *et al.*, *Nature*, 1949, **164**, 1095
[76] Beckley, ibid., 1948, **162**, 737
[77] Idem, *E. Afric. agric. J.*, 1948, **14**, 71
[78] Idem, *Pyrethrum Post*, 1948, **1**
[79] Idem, *Chem. Age*, 1948, **59**, 398
[80] Bovingdon, *Nature*, 1949, **163**, 731
[81] Kulash, *J. econ. Entom.*, 1948, **41**, 715
[82] *Chem. Age*, 1949, **61**, 211
[83] Stoker, *Ann. appl. Biol.*, 1948, **34**, 110
[84] *Nature*, 1948, **162**, 845
[85] Hocking, ibid., 1949, **163**, 731
[86] *J. econ. Entom.*, 1948, **41**, 865
[87] IInd Int. Congr. Crop Protect. Lond., 1949, Abs. Comm.
[88] *1st botan. univ. lab crittogam. Pavia Att.*, 1947, **3**, 291
[89] *Nature*, 1949, **163**, 608
[90] *Indian Archives*, 1949, **5**, (in press)
[91] *Ann. appl. Biol.*, 1949, **36**, 76
[92] Way and Synge, *Ann. appl. Biol.*, 1948, **36**, 94
[93] Smith *et al.*, *J. econ. Entom.*, 1948, **41**, 960
[94] Ibid., 1949, **42**, 7
[95] *Brit. J. Pharmacol.*, 1949, **4**, 120
[96] *J. chem. Soc.*, **1948**, 1657
[97] *J. econ. Entom.*, 1949, **42**, 116
[98] *Anz. Schädlingskunde*, 1949, **22**, 3
[99] *Riv. parasitol. (Roma)*, 1948, **8**, 127
[100] *J. econ. Entom.*, 1948, **41**, 802
[101] *Riv. parasitol. (Roma)*, 1947, **8**, 127
[102] Ibid., 1948, **9**, 137
[103] Bettini and Baradrini, *Rend. ist. super sanità.*, 1948, **11**, 841
[104] *Pyrethrum Post.*, 1949, **1**, 32
[105] Blackith, R. E., forthcoming publication
[106] Gorringe, B. S., Imperial College of Science and Technology, priv. comm.
[107] Gunn *et al.*, Anti-Locust Bull. No. 3, Anti-Locust Res. Centre, Lond., 1949
[108] Idem, ibid., No. 4
[109] Gunn, *Nature*, 1948, **162**, 308
[110] Hopf, Second Inter. Congr. Crop Protect., Lond., 1949
[111] Way and Stoker, *Ann. appl. Biol.*, in press
[112] Way, ibid., 1949, **36**, 86
[113] Way and Stoker, ibid., (in press)
[114] *Ann. appl. Biol.*, 1947, **34**, 586
[115] Ibid., 1948, **35**, 527
[116] Mackintosh, priv. comm.
[117] *Physiol. Zool.*, 1948, **21**, 48
[118] *Ind. Eng. Chem. (Anal. Ed.)*, 1945, **17**, 704
[119] Page, A. B. P. *et al.*, *Ann. appl. Biol.*, 1949, **36**, 225
[120] *Proc. roy. Soc.* 1946 [B], **133**, 407
[121] *Discuss. Faraday Soc.*, 1948, **3**, 193
[122] *Biol. Rev.*, 1948, **23**, 408; *Ann. Rev. Biochem*, 1949, **28**, 595
[123] *Trans. Faraday Soc.*, 1948, **44**, 60
[124] *J. exp. Biol.*, 1945, **21**, 97
[125] Lees, ibid., 1947, **23**, 397
[126] *Nature*, 1948, **162**, 296

[127] *Nature*, 1949, **163**, 769
[128] Ibid., 109
[129] Etherington, ibid., **164**, 32
[130] Page, A. B. P., Annual Reports, 1948, **33**, 435
[131] *J. Soc. chem. Ind.*, 1946, **65**, 357
[132] *Nature*, 1946, **158**, 22
[133] *Ann. appl. Biol.*, 1948, **35**, 505
[134] Ibid., 1949, **36**, 113
[135] *Biochem. J.*, 1948, **43**, 72
[136] *Ann. appl. Biol.*, 1949, **36**, 206
[137] Martin, H. and Wain, R. L., *Nature*, 1949, **163**, 918
[138] IInd Internat. Congress of Crop Protection, 1949
[139] Stringer, *Ann. appl. Biol.*, 1949, **36**, 213
[140] Woodcock, *J. chem. Soc.*, **1949**, 203
[141] *Arquiv. Inst. Biol., Sao Paulo*, 1948, **18**, 135
[142] *Soap*, 1949, **25**, 129
[143] Gersdorff, *J. econ. Entom.*, 1949, **42**, 532
[144] *Nature*, 1949, **163**, 496
[145] *Ann. appl. Biol.*, 1949, **36**, 153
[146] Unterstenhöfer, *Hofchen Briefe.*, 1948, **1**, 20
[147] *Ann. appl. Biol.*, 1949, **36**, 156
[148] Ibid., 160
[149] *Mfg. Chem.*, 1949, **20**, 158
[150] *Nature*, 1950, **165**, 100
[151] Dvornikoff and Morrill, *Analyt. Chem.*, 1948, **20**, 935
[152] Bowen and Edwards, quoted by Haller, *Soap*, 1949, **25**, 127
[153] Ibid., 1948, **20**, 753
[154] Edwards, ibid., 1949, **21**, 1415
[155] Jones, quoted by Haller, *Soap*, 1949, **25**, 127
[156] Davidson and Jernell, quoted by Haller, ibid.
[157] Zotta and Semló, *Rev. Brasil. quim.*, 1949, **27**, 242
[158] Edwards and Hall, *Analyt. Chem.*, 1949, **21**, 1567
[159] Grodsky, ibid., 1551
[160] Marrison, L. W., *J. Soc. chem. Ind.*, 1949, **68**, 192
[161] Davidson, quoted by Haller, *Soap*, 1949, **25**, 127
[162] *Analyt. Chem.*, 1947, **19**, 779
[163] Ibid., 1949, **21**, 285
[164] Cupples, ibid., 630
[165] Aepli *et al.*, ibid., 1948, **20**, 610
[166] Bowen and Pogorelskin, ibid., 346
[167] Carter, quoted by Haller, *Soap*, 1949, **25**, 127
[168] *Analyt. Chem.*, 1948, **20**, 241
[169] Bull. No. 32, 5, 1948 (Dec. 31)
[170] Ingram and Southern, *Nature*, 1948, **161**, 437
[171] Dragt, *Analyt. Chem.*, 1948, **20**, 737
[172] Haller, *Soap*, 1949, **25**, 127
[173] Shirley *et al.*, *J. Amer. chem. Soc.*, 1949, **71**, 3173
[174] *Arch. exp. Path. Pharmacol.*, 1948, **205**, 223
[175] Truhaut and Vincent, *C.R. Acad. Sci., Paris*, 1948, **227**, 738
[176] Picard and Kearns, *Canad. J. Res.*, 1949, **27**D, 59
[177] U.S. Dept. Agr. Bull., 1948
[178] *Pharmazie*, 1949, **4**, 165
[179] *Proc. Amer. Soc. hort. Sci.*, 1948, **51**, 327
[180] *Agric. Chem.*, 1949, **4**, 35
[181] *Soil Sci. Soc. Amer. Proc.*, 1948, **12**, 227
[182] *Proc. Amer. Soc. hort. Sci.*, 1948, **51**, 196
[183] *J. econ. Entom.*, 1948, **41**, 616
[184] *Agric. Chem.*, 1949, **4**, 75
[185] Lehner *et al.*, *J. Animal Sci.*, 1949, **8**, 141
[186] *J. econ. Entom.*, 1948, **41**, 875
[187] Savage *et al. Chem. Industr.*, 1949, **64**, 392
[188] *Z. Naturf.*, 1947, **2B**, 245

[189] *J. econ. Entom.*, 1949, **42**, 44
[190] *J. Dept. Agr. S. Austr.*, 1947, **51**, 6
[191] Breakey and Bachelor, *J. econ. Entom.*, 1948, **41**, 987
[192] *Nature*, 1948, **162**, 181
[193] Ibid., 1949, **163**, 723
[194] Burgoyne and Thomas, ibid., 765
[195] Burgoyne and Williams-Leir, *Proc. roy. Soc.*, 1948 [A], **193**, 525
[196] Lichtenstein and Twigg, *Trans. Faraday Soc.*, 1948, **44**, 905
[197] Gupta, A. K., *J. Soc. chem. Ind.*, 1949, **68**, 179
[198] Page, A. B. P., Lubatti, O. F. and Russell, J., ibid., 102
[199] Page, A. B. P. and Lubatti, O. F., ibid., 151
[200] *Ann. appl. Biol.*, 1950, **37**, in press
[201] Priv. comm.
[202] Ibid.
[203] *J. Helminthology*, 1948, **22**, 117
[204] Ibid., 128
[205] Ibid., 1949, **23**, 73
[206] *Ann. appl. Biol.*, 1949, **36**, 364
[207] *Agriculture*, 1949, **55** 493
[208] *J. roy. Lancs. agric. Soc.*, 1949 Annual Journal
[209] *Proc. helminth. Soc. Wash.*, 1949, **15**, 43
[210] Priv. comm.
[211] IInd Int. Congr. Crop Protect., Lond., 1949, Abs. Comm. 96
[212] *Phytopathology*, 1947, **37**, 440
[213] Call, priv. comm.
[214] 'Control of Insects in Dried Fruit,' D.S.I.R. Pamphlet (H.M.S.O.: 1942)
[215] *J. econ. Ent.*, 1948, **41**, 804
[216] *Hilgardia*, 1942, **19**, 373
[217] 'Désinsectization par fumigation avec vide préalable,' Document Phytosanitaire, No. 9 du Ministère de l'Agriculture (Alger.: 1949)

ESSENTIAL OILS, ISOLATES AND DERIVATES

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CERTAIN aspects of the literature of essential oils have been brought up to date by the publication of two further volumes of "The Essential Oils," by E. Guenther.[1] Volume II deals with constituents, their chemistry, isolation and uses, and includes a section on the preparation of derivatives of essential oil constituents which are employed for purposes of identification. Volume III contains a series of monographs on the individual oils of the families Labiatæ and Rutaceæ. In a book entitled "Citrus Products," J. B. S. Braverman[2] gives details of the extraction and analysis of citrus oils. The 1946 Report issued by Schimmel Co. Inc.[3] of New York maintains the standard set by its predecessor of last year and will prove a useful work of reference. Guenther and Langenau,[4] in a review article of recent publications, include specifications and methods of assay, also brief notes on analytical methods, with a bibliography. Following on the publication last year of the British Pharmacopœia is the British Pharmaceutical Codex, 1949[5] which includes one new oil monograph covering melaleuca (ti-tree) oil. There are, however, 11 deletions of oils which are considered to be of little medicinal importance—these are ajowan, bitter almond, copaiba, cumin, terpeneless lemon and nutmeg, spearmint, parsley, pennyroyal, rue and savin.

Development of the essential-oil industry in various parts of the world is the theme of a number of authors. Penfold[6] reviews the part which the Museum of Technology, Sydney, is playing in shaping the future of the industry in Australia. Attempts are being made to find practical applications for the unique constituents of local oils. The development of methods is in hand for controlling the composition of the oils from physiological forms of the plants and the utilization of these methods for the development of new varieties. Whereas in the past the crude oils have been exported, efforts are now being made to isolate the constituents and to utilize these for the manufacture of useful products in Australia. India continues to focus attention on the oils of its native flora. Chopra *et al.*[7] contribute notes on some Kashmir plants, including the physical characters of the oils of *Acorus calamus*, *Cinnamomum tamala*, *Hyssopus officinalis*, *Angelica glauca*, *Salvia moorcraftiana*, *S. glutinosa*, *S. dumetorum*, *Eschscholtzia cristata*, *E. densa*, *Heracleum cachemiricum*, *Artemisia dracunculus*, *A. laciniata*, *A. amygdalina*, *A. grata*, *A. parviflora*, *Macrotomia benthami*, *Rhus succedeana*, and *Vitex negundo*. The results of cultivation experiments on South Indian vetiver root in and around fish-curing yards of the west coast are reported.[8] The scheme was to study optimum conditions for the maximum yield of oil per acre. The optimum period of growth was found to be 15 to 18 months; manuring with ammonium sulphate, brine manure and groundnut cake increased

the yield of oil, which varied between 0·10 and 1·02%. Narain *et al.*[9] examined 16 samples of vetiver oil from various sources and found that the Indian oils had higher ester- and acetyl-values than those of Reunion, Java or Singapore : this is considered to be the reason for the better odour of the Indian product. These authors quote limits for the characters of genuine Indian oil. Before the war vetiver oils were often adulterated with copaiba balsam oil and sometimes with castor oil, but the common practice now is to add sandalwood oil. The effect of various additions of sandalwood oil is tabulated. A useful memorandum is published in the Bulletin of the Imperial Institute[10] showing the annual exports of essential oils from our various colonies from 1938 onwards. The 21 oils listed as separate items in trade returns are dealt with in detail, including uses and future possibilities. Attention is directed also to the possibility of development of five oils—bois-de-rose, lavender, neroli, peppermint and vetiver—which are not mentioned in colonial trade returns.

Palestinian oils, particularly those from citrus fruits, are referred to in a number of papers. Feigenbaum[11] publishes a review of the methods of production, yields and characters of oil of lemon, orange, grapefruit and neroli. The yields quoted are : lemon, 1·5–2·0 kg. per ton ; orange about 2·5 g. ; grapefruit about 1 kg. and orange flowers about 0·01%. Two reports from the Imperial Institute deal with grapefruit[12] and orange[13] oils from this source. In a most interesting account, Hardy[14] mentions a number of aromatic plants recorded by himself when botanizing in Palestine. Special emphasis is laid upon the Labiates which develop their full fragrance on the hot dry hillsides, where the oil vapour surrounds the plants, thus reducing the evaporation of water from the leaves. The lost scent of the musk plant (*Mimulus moschatus*) is discussed. It is explained that the original musk plant was a native of semi-tropical California, where the scent is required to keep the plant cool and to reduce transpiration. When transplanted to England, the wet climate no longer demanded the secretion of oil and thus it gradually lost its odour. When these plants in turn were transplanted to their native North America and to Palestine they could no longer protect their leaves against excessive transpiration and they eventually died. In a bulletin from the University of Florida[15] commercial methods of production of citrus oils are described and compared, and the fact that the quality of these oils is influenced by the quantity of aqueous phase coming in contact with them during processing is confirmed. In an attempt to develop high oil-yielding strains of garden sage, Drain *et al*[16] made selections on vegetative characters ; the best were further selected on the basis of oil content. The highest assaying strains varied from 1·6 to 3·25% of oil on an air-dry basis.

A review of the wormwood industry[17] in Michigan and Indiana states that the plants last for 7–10 years from a single planting and the yield is from 15–20 lb. of oil per acre. In Maryland and California coriander seed[18] from 17 different sources was grown over a period of five years for observations regarding plant types, growth, fruiting habits and yield of essential oil. It was found that there were two distinct types of plant : one was early maturing, short and bushy while the other was later maturing, taller and less branching. The early type produced seed of better

appearance but the later type, though of poor appearance, was richer in essential oil; this accounts for the fact that Russia and Hungary, where the later type is grown, are the principal producers of the oil. Loustalot[19] has experimented in Porto Rico with fertilizer treatments on bay plants. Ammonium sulphate alone or in combination with potassium or phosphorus increased the yield of fresh vegetative growth, but the value of the additional oil obtained by treatment with ammonium sulphate amounted to only about half the cost of the fertilizer. A serious effort has been made to establish an essential oil industry in the Georgian Republic of the U.S.S.R.[20] which has a rich soil and a sub-tropical climate. The Suhum Zonal Experimental Station has developed a new variety of pelargonium yielding three times as much oil as the rose geranium hitherto employed. Rose, *Ocimum basilicum*, patchouli, tuberose and jasmin are also cultivated. Gattefossé and Igolen[21] describe a number of Moroccan aromatic plants and their oils; they include: *Mentha rotundifolia, M. longifolia* var. *candicans*, *Pulicaria mauritanica*, *Satureja peltieri*, *Juniperus oxycedrus*, *Ammi visnaga*, *Glycyrrhiza fœtida*, *Salvia maurorum*, *Mentha rotundifolia* (*M. timija*) and the Moroccan chamomile. Owing to the warm autumn of 1945 the bitter orange trees in Alpes-Maritimes[22] flowered; flowers again appeared in April, 1946, and the oil distilled from them had a lower specific gravity, lower refractive index, a higher ester value, and contained less methyl anthranilate and indole than normal oil.

Efforts are being made to find outlets for 'by-product distilled citrus oil' in the U.S.A. and an account of this oil, which is obtained from mixed citrus cannery waste during the production of citrus molasses for cattle feed, is published by Bell.[23] Samples examined were from 50,000 gal. of oil produced during one year by three citrus feed mills. A typical analysis was $d_{25°}$, 0·843; $[\alpha]_D^{25°}$ + 97·65°; $n_D^{25°}$, 1·4703; acid value 0·8; ester value 1·7; aldehyde (as decylic) 0·4%, and evaporation residue 0·12%.

Two groups of antioxidants were studied with Florida cold-pressed orange oil.[24] Each group contained five antioxidants, which were added singly and in every possible combination of pairs, in amounts giving a total concentration of 0·1%. Four were proprietary antioxidants and the remaining six were: ethyl caffeate, ascorbic acid, citric acid, α-tocopherol, *iso*thymol and nordihydroguaiaretic acid; α-tocopherol was found to be the most effective. Fesneau[25] reports on the occurrence of contact dermatitis in at least a dozen workers with Java citronella oil over the last 20 years and is of the opinion that citronellal is the cause of the trouble. In a U.S. patent[26] claims are made for the solubilization of essential oils by dissolving them in water-soluble hydroxy-polyethylene ethers of aliphatic mono-carboxylic fatty acid esters of polyhydric alcohols such as ethylene glycol, glycerol, pentaerythritol, mannitol, sorbitol, etc.; the fatty acid is preferably a C_{12}–C_{16} acid.

The Essential Oil Association of the U.S.A.[27] has prescribed methods for the determination of acid value, evaporation residue and chlorinated compounds. Standards are also laid down for 19 substances which include safrol, cajeput, patchouli, vetiver, palmarosa, grapefruit, spruce and cedarwood oils. Determination of the evaporation residue is carried out in a 100-c.c. glass evaporating dish on a steam bath; unfortunately

the diameter of the dish is not specified. The test for chlorinated compounds is a limit test, no actual determination being carried out.

Composition and characters

Acorus calamus L.[28]—The sesquiterpene fractions of the oil of Dutch origin were investigated and the characteristic odour was found to be due to (+)-camphor, terpene alcohols and an aldehyde. Calamene was considered to be a mixture of 80% of a bicyclic and 20% of a tricyclic sesquiterpene α- and β-calamene. Other new compounds isolated were acoroxide $C_{15}H_{24}O$ and three ketones: calamone, acorone and *iso*acorone.

Anethum sowa, Roxb.[29]—From an examination of 80 samples Hossain and Mukerji suggest, as standards: appearance, colourless to light-yellow or light-brown; *d*, 0·920–0·950; $[\alpha]_D$, + 47° to + 60°; n_D, 1·480–1·495; carvone, 40–55%.

Boronia ledifolia Gay.[30]—A new physiological form of this Australian plant is differentiated from others of the same species by the presence in the essential oil of about 75% of methyl heptyl ketone and methyl nonyl ketone.

Callitris articulata (Valhl.) Murbeck.[31] (Barbary thuya.)—From the leaves and young shoots of this Moroccan plant the authors obtained 1% of a yellow oil, the principal constituents of which were (+)-α-pinene, (+)-borneol and bornyl acetate.

Callitris glauca R.Br.[32]—The wood oil of the cypress pine was found to contain, in addition to large amounts of (−)-citronellic acid, about 2% of 2 : 6-dimethyl-*n*-hepta-1 : 3 : 5-triene-1-carboxylic acid (m.p. 186-187° c.) and a number of unsaturated acids giving colour reactions with Br and with H_2SO_4.

Cistus ladaniferus L.[33]—The fresh leaves from plants growing in Spain yielded 0·1 to 0·2% of oil. New constituents detected were diacetyl, furfuraldehyde, (−)-pinene, cineole and borneol.

Citrus sinensis (L.) Osbeck.[34]—A benzol extract of sweet orange leaves was found to contain aldehydes 16%, free primary and secondary alcohols 8%, total alcohols 14·5% and esters 9·5%. Steam distillation separated the extract into a waxy residue and a yellow volatile oil which had a more delicate odour than the original.

Conifer leaf oils.[35]—In a report on leaf oils from conifers of the Tennessee Valley, yields, characters and constituents of 26 species are given.

Costus oil.[36]—Naves gives a general account of the oil and its constituents together with a useful range of characters determined by himself.

Eucalyptus citriodora.[37]—A physiological form of this species yielded an oil in which the principal constituents were citronellol and its esters instead of citronellal. The characters of this oil were: *d*, 0·8898; n_D, 1·4580; $[\alpha]_D$+ 2·7°; citronellal, 7%.

Eucalyptus globulus.[38]—The ketones carvone, pinocarvone, verbenone and myrtenal were identified in the Spanish oil, also a five-ring ketone, 3 : 1-acetyl*iso*propylidene*cyclo*pent-5-ene, not previously found in natural oils.

Geranium macrorrhizum L. 'Zdravets.'[39]—Naves compares the oil of Bulgarian origin with that produced in Cyprus. The Bulgarian oil is semi-solid owing to the presence of crystals of a sesquiterpene oxide, germacrol ($C_{15}H_{22}O$). The plant grown in Cyprus yields from 0·10–0·15% of a slightly viscous oil which is olive green in colour and has an odour very similar to that of geranium oil (Pelargonium sp.) The oil contained ketones, mostly (−)-*iso*menthone 28·1%; free alcohols 36%; total alcohols 55·2%; apparent rhodinol 52·6% and esters 24·4%. Subsequently [40] specimens of the Cyprian plants were found not to be *G. macrorrhizum* but a species of *Pelargonium.*

Lavandula spica D.C.[41]—Three new constituents were found in this oil: *n*-hexanol-1 to the extent of 0·03–0·04%; coumarin 0·05%; and formic acid 0·01–0·02%.

Ledum palustre.[42]—The fresh leaves yielded 0·7–1·6% of essential oil having d, 0·9085; n_D, 1·4882; $[\alpha]_D - 12{\cdot}5°$. On chilling ledol ($C_{15}H_{26}O$), a saturated sesquiterpene tertiary alcohol separated. The higher-boiling fraction of the filtrate contained up to 70% or more of alcohols including a new tertiary tricyclic sesquiterpene alcohol, palustrol ($C_{15}H_{26}O$).

Libocedrus bidwillii, 'New Zealand Cedar.'[43]—The autumn oil obtained by steam distillation of leaves and terminal twigs in a yield of 0·29% was fractionated. 15 constituents were separated: (−)-α-pinene, (+)-sabinene, myrcene, a ketone ($C_{10}H_{16}O$), limonene and dipentene, *p*-cymene, terpinolene, terpinen-4-ol, a tricyclic sesquiterpene, a sesquiterpene, caryophyllene, γ-curcumene and (+)-cadinene.

Melaleuca alternifolia, Cheel.[44]—Samples of the foliage of this Australian tree were collected from 49 plants distributed over a wide area. The distilled oils were examined for optical rotation and cineole content. The two figures showed excellent correlation; thus, determination of the rotation offers a quick means of estimating the cineole content. It was found possible to classify the trees into three groups according to the cineole content of their oils: a 'low' cineole group from 6–14%, a 'medium' group from 31–41% and a 'high' group from 54–64%.

Melaleuca bracteata F.v.M. (from Kenya).[45]—Leaves and terminal twigs of young trees, grown from New South Wales seed, yielded 0·5% of oil. Apart from specific gravity, the oil had constants which were in fair agreement with those of Australian oils. The oil closely resembled Huon pine oil in that it contained about 82% of methyleugenol. Mitchell[46] examined a sample of oil from the same source but distilled it a year later and found it to contain 75% of methyleugenol. It was considered to be of little commercial interest since methyleugenol can be prepared readily from other sources of eugenol.

Mentha cardiaca Gerarde.[47]—The fresh plant yielded 0·477% of oil (59 lb. per acre) of spearmint odour. The cohobated aqueous distillate yielded an oil constituting 8% of the total oil. The average carvone content of the combined oils was 59%. Hocking[48] reports that in addition to true spearmint (*M. spicata* L.) an increasingly large proportion of the commercial herb and oil produced in the U.S.A. is derived from Scotch spearmint (*M. cardiaca* Gerarde): this plant is more prolific and yields a higher proportion of oil than spearmint, but it is less hardy and rather more prone to insect and fungal attack.

Mentha gattefossei Maire.[49]—A new pulegone mint of Morocco is described. The oil contained 87% of pulegone.

Mentha piperita L.[50]—Several hitherto undetected constituents are reported in American, Russian, Italian and Bulgarian oils: jasmone, caryophyllene, a sesquiterpene ketone, $C_{15}H_{24}O$; a sesquiterpene alcohol $C_{15}H_{26}O$, a bicyclic sesquiterpene, $C_{15}H_{24}O$, and a free and esterified octene-carboxylic acid. The American oil contained a high proportion of menthofuran.

Nepeta cataria L.[51]—The leaves and flowering tops of catnip herb yielded about 0·3% of volatile oil. This oil may be identified by treating a drop on a microscope slide with a drop of phenylhydrazine. Characteristic birefringent crystals develop within 15 minutes.

Palmarosa oils, Indian.[52]—The characters of palmarosa oil (Motia) and gingergrass oil (Sofia) have been determined. The former had a total geraniol content of 78–94%, and the latter, 60–75%.

Pectis papposa.[53]—The oil from the fresh plant was obtained in a yield of 0·4–0·6% and the dried plant 0·5–1·88%. It contained cuminaldehyde 50%, ketones 25% (probably pinocarvone 20%, carvone 5%), a terpene hydrocarbon 25% (probably β-pinene).

Pimenta racemosa.[54]—Childers *et al.* give an account of the bay oil industry in Porto Rico.

Gum terpentines.[55]—The physical and chemical properties of turpentines from five species of pine have been determined: *Pinus strobus, P. cembra, P. taeda, P. radiata* and *P. virginiana.* The composition of *P. lambertiana* turpentine has been determined,[56] but contrary to the work of Schorger[56a] neither phellandrene nor an aliphatic hydrocarbon was found.

Rumanian pine oils.[57]—A study has been made of oil from needles of *Abies alba, Picea excelsa* and *Pinus sylvestris.* The quality of the Rumanian oils was considered to rank with Siberian fir oil and similar European and American oils.

Pittosporum eugenoides.[58]—Leaves of this New Zealand tree yielded 0·07% of essential oil, which was remarkable for its high content (60%) of a liquid paraffin identified as *n*-nonane. It also contained three other paraffins of melting points 44·5°, 56° and 63° c., respectively, sabinene, limonene, an aldehyde, a crystalline glycol (resembling *p*-menthane-3 : 8-diol), *p*-menthane-3 : 4-diol and β-pinene glycol.

Pittosporum tenuifolium.[59]—Leaves and terminal twigs yielded 0·134% of a blue oil from which the following constituents were isolated: (+)-α-pinene, (+)-β-pinene, myrcene, dipentene and (+)-limonene, β-terpinene (reported for the first time as a constituent of essential oils), a terpene aldehyde, (−)-bornyl acetate, a sesquiterpene, a bicyclic and a tricyclic sesquiterpene, guaiazulene, solid paraffins and unidentified sesquiterpene alcohols and diterpenes.

Pycnanthemum pilosum Nutt.[60]—The fresh plant yielded 0·95–0·976% of oil, and in a preliminary report the physical characters are recorded. The presence of phenols was indicated and pulegone was isolated. The aqueous cohobate contained an alcohol and an aldehyde or ketone.

Raphanus sativus L., var. *alba.*[61]—A glycoside obtained by extraction of the seeds with acetone was converted by aqueous silver nitrate and

then sodium thiosulphate into the optically active *iso*thiocyanate, 1-methylsulphinyl-4-*iso*thiocyano-*n*-but-1-ene. An additional product[62] was obtained, by partition chromatography on SiO_2 gel, of the fission products of the glycoside, 4-methylsulphinyl-1-cyanobut-3-ene.

Sassafras oil, Brazilian.[63]—The freshly distilled oil had the characters: d, 1·076; n_D, 1·5350; $[\alpha]_D - 1{\cdot}42°$; congealing point 9·0° c.; acid value 0·3; ester value 5·0; ester value, after acetylation 9·0; aldehyde content less than 0·1%; safrole 92·9; α-pinene 0·7; eugenol 0·6; furfuraldehyde 0·17 and cineole 0·21%.

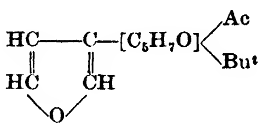
Solidago odora, 'Sweet Golden Rod.'[64]—This Texan plant and its essential oil are described and the characters recorded. The oil contained 75% of methylchavicol and had an anise-like odour and flavour.

Isolates and derivatives

Naves[65] advocates the use of the Raman effect in the study of the isomers of citronellol, citronellal, geraniol, linalool and similar compounds; he also answers the critics of the method. During a study of considerable quantities of authentic French Guinea oil, Benezet and Igolen[66] found the mixed aldehydes to contain from 75–80% of *n*-octylic aldehyde together with decylic and nonylic aldehydes.

In the tailings of American, Russian, Japanese, Italian and Bulgarian peppermint oils jasmone[67] was found to be present to the extent of 0·1% or less. Jasmone is believed to be an important odoriferous constituent of the oils. American oil was rich in menthofuran. Naves[68] in a communication to the Scientific Section of the Toilet Goods Association in New York gave an account of work so far on the structures and syntheses of the irones. An azulene[69] identical with vetivazulene, having a m.p. of 31·5–32·0° c. has been isolated from elemi oil.

Ngaione[70] was obtained in 80% yield by fractionation of the oil of the leaves and terminal branches of the New Zealand plant *Myoporum laetum* Forst. This ketone, $C_{15}H_{22}O_3$, was shown to have the partial structure



incorporating 3-furyl, acetyl and *iso*butyl groups and a residue C_5H_7O.

Chenopodium oil[71] was fractionated to prepare pure ascaridole. Its properties and the ultra-violet absorption spectrum were studied.

Analytical

Several workers have reported on methods of determining aldehydes in essential oils. Halpern[72] discusses the advantages and disadvantages of the five methods: bisulphite absorption, neutral sulphite, phenylhydrazine, hydroxylamine and fuchsin sulphite. Rao[73] proposes a modification of the British Pharmacopœia method by titrating the acid liberated when an alcoholic solution of hydroxylamine hydrochloride reacts with the aldehyde. Fuchs and Matzke[74] have applied the method of

titration against hydrazine salts to benzaldehyde, vanillin and piperonal. The hydroxylamine hydrochloride method for the determination of aldehydes, ketones and acetals has been investigated by Maltby and Primavesi[75] and a satisfactory technique is described. Although the authors do not appear to have used the method on essential oils there seems to be no reason why it should not be applicable.

Mori[76] has developed a method for the determination of anethole in anise oil, depending upon the fact that anethole in solution in benzene is quantitatively converted by iodine chloride in the presence of potassium iodide into 1 : 2-di-iodopropyl-*p*-methoxybenzene. The unreacted iodine chloride is quantitatively converted into free iodine which is titrated with excess of thiosulphate and back titrated with iodine. The congealing points of known anethole–limonene mixtures have been determined and tabulated by Fritzsche Bros. Inc.[77] The congealing point was found to be a function of the anethole content and proportional to it. The curve within the concentrations of 55 and 100% w/w was a straight line.

Lepetit[78] in a thesis includes an examination of the various published methods for the determination of ascaridole, the iodimetric method being favoured. The final recommended method is based on that of the French Codex which differs from the B.P. assay in several minor details. The factor 0·00605 for converting the ml. N/10-thiosulphate into ascaridole is suggested. The B.P. factor is 0·00665 and the present French Codex figure is 0·0084.

A study has been made by Julien[79] of the existing methods for determination of camphor in the three main types of galenical preparation, and the following are recommended : (i) weak and strong tinctures of camphor—Janot and Mouton's method using 2 : 4-dinitrophenylhydrazine[79a]; this is a modification of the B.P. method ; (ii) camphorated oil—the method of Leonard and Smith[79b]; (iii) ammoniated liniment of camphor and camphor ointment—Leonard and Smith's method as given in the B.P. No satisfactory method was found for *Tinct. Opii Camph.*

For the determination of menthone in mint oils, Hoffmann[80] refluxes the oil with aqueous-alcoholic hydroxylamine and the excess titrated with hydrochloric acid, or the oil is shaken with cold aqueous-alcoholic hydroxylamine hydrochloride and the liberated acid titrated with potash. The lower results obtained by the cold method suggest that oxime formation is not complete ; concordant results are obtained by the hot method.

Methyl anthranilate and indole have been determined by Maurel[81] by shaking the oil with dilute alcohol ; an aliquot part of the solution is diazotized by boiling with sodium nitrite and acetic acid. The reddish-orange colour obtained with an ammoniacal solution of R acid is compared with standard solutions of methyl anthranilate. Indole is determined by treating another aliquot with *p*-dimethylaminobenzaldehyde and the reddish-orange colour is compared with standards.

The distillation method for the determination of safrole is criticized by Messrs. Salamon and Seaber,[82] who prefer to use a freezing point method by seeding with a trace of solidified safrole. As a tentative standard they suggest a lower limit of 8° C. Littlejohn[83] quotes details of the cryoscopic method of the Technical Secretariat of Brazil as reported by the International Standards Organization.

A method is described by Langenau[84] for the separation of phenols from thyme oils. If the phenols separated from Spanish thyme oil crystallize at 20° C. after seeding, the phenols of the original oil consist of more than 40% thymol, and the oil cannot be of the carvacrol type. If the phenols crystallize within 5 minutes at 0° C. when seeded, then the phenols contain more than 20% thymol.

A most useful table of flash points of essential oils and isolates determined in the Pensky–Martens apparatus has been compiled in the laboratories of Variochem V.V.B. Schimmel.[85] A rapid method of conversion from sp.gr. at 15·5° C. to wt. per ml. is described by A. Mc. M. Taylor.[86]

A continuous distillation apparatus[87] for the determination of essential oil in leaves, etc., is described by McKern and Smith-White. It is claimed that distillations in which equal weights of leaves and water are used are practically complete in 4–12 hours.

References

1 Guenther, E., "The Essential Oils," Vol. II & III, (New York, D. Van Nostrand & Co. Inc., 1949)
2 Braverman, J. B. S., "Citrus Products" (New York, Interscience Publishers, Inc., 1949)
3 Schimmel Report, 1946, Schimmel & Co. Inc., New York
4 Guenther, E. and Langenau, E. E., *Analyt. Chem.*, 1949, **21**, 202
5 "British Pharmaceutical Codex" (London, Pharmaceutical Press, 1949)
6 Penfold, A. R., *Soap Perf. and Cosmetics*, 1949, **22**, 842
7 Chopra, I. C., Handa, K. L. and Kapoor, L. D., *Indian J. agric. Sci.*, 1947, **17** (2), 100
8 Murti, K. S. and Raman Moosad, C., *Amer. Perfum.*, 1949, **54**, 113
9 Narain, Goswami and Das Gupta, *Indian Soap J.*, 1949, **14**, 303
10 Islip, H. T., *Bull. Imp. Inst., Lond.*, 1948, **46**, 159
11 Feigenbaum, J., *Industr. de la Parfum.*, 1949, **4**, 37
12 Islip, H. T. and Major, F., *Bull. Imp. Inst., Lond.*, 1948, **46**, 215
13 Idem, ibid., 213
14 Hardy, E., *Perfum. essent. Oil Rec.*, 1949, **40**, 43
15 Kesterson, J. W. and McDuff, O. R., *Univ. Florida agric. exp. Sta. Bull.*, **1948**, 452
16 Drain, D. B., Overcash, J. P., Hanchey, R. H. and Downey, A. H., *Proc. Amer. Soc. hort. Sci.*, 1949, **53**, 371
17 *Chemurgic Digest*, Jan., 1949
18 Lowman, M. S., Gilbert, N. W. and Kelly, J. W., *Amer. Perfum.*, 1949, **54**, 209, 300
19 Loustalot, A. J., *Proc. Amer. Soc. hort. Sci.*, 1949, **53**, 517
20 *Chemist and Druggist*, 1949, **151**, 479
21 Gattefossé, J. and Igolen, G., *Industr. de la Parfum.*, 1949, **4**, 110
22 Maurel, A., ibid., 4
23 Bell, S. A., *Perfum. essent. Oil Rec.*, 1949, **40**, 205
24 Kesterson, J. W. and McDuff, O. R., *Amer. Perfum.*, 1949, **54**, 285
25 Fesneau, M., *Perfum. essent. Oil Rec.*, 1949, **40**, 295
26 U.S.P. 2,422,145
27 *Perfum. essent. Oil Rec.*, 1949, **40**, 10
28 Šorm, F. and Herout, V., *Coll. Trav. chim. Tchécosl.*, 1948, **13**, 177
29 Hossain and Mukerji, *Indian Pharm.*, 1946, 169
30 Penfold, A. R. and Morrison, F. R., *J. Proc. roy. Soc., N.S.W.*, 1948, **82**, 71
31 Gattefossé, J. and Igolen, G., *Industr. de la Parfum.*, 1949, **4**, 35
32 Newhaus, J. W. G. and Reuter, F. H., *J. Aust. chem. Inst.*, 1948, **15**, 185
33 *Perfum. essent. Oil Rec.*, 1949, **40**, 421
34 Gottlieb, O. R., *Industr. de la Parf.*, 1949, **4**, 9
35 Bailey, L. F., *J. For.*, 1948, **46**, 882
36 Naves, Y. R., *Mfg. Chem.*, 1949, **20**, 318
37 Penfold, A. R. and Morrison, F. R., *Aust. J. Sci.*, 1948, **11**, 29

[38] Schmidt, H., *Chem. Ber.*, 1947, **80**, 528
[39] Naves, Y. R., *Perfum. essent. Oil Rec.*, 1949, **40**, 161
[40] Idem, ibid., 391
[41] Girard, *Industr. de la Parfum.*, 1949, **4**, No. 7
[42] Kiryalov, N. P., *Doklady Akad. Nauk, U.S.S.R.*, 1948, **61**, 305, through *Chem. Abstr.*, 1949, **43**, 1155
[43] Batt, R. D. and Hassell, C. J., *J. Soc. chem. Ind.*, 1949, **68**, 359
[44] Penfold, A. R., Morrison, F. R. and McKern, H. H. G., *Perfum. essent. Oil Rec.*, 1949, **40**, 149
[45] Cosgrove, D. J., Islip, H. T. and Thain, E. M., *Bull. Imp. Inst., Lond.*, 1948, **46**, 46
[46] Mitchell, W., ibid., 50
[47] Ballentine, K. D. and Schwarting, A. E., *J. Amer. pharm. Assoc., Sci. Ed.*, 1949, **38**, 241
[48] Hocking, G. M., ibid., 394
[49] Gattefossé, J., Benezet, L. and Igolen, G., *Industr. de la Parfum.*, 1949, **4**, 11
[50] Schmidt, H., *Chem. Ber.*, 1947, **80**, 538
[51] Greene, L. W., *Amer. J. Pharm.*, 1949, **121**, 91
[52] Narian, K. and Das Gupta, P. N., *Indian Soap J.*, 1948, **13**, 259
[53] Bradley, C. E., *Drug Cosmetic Industr.*, 1949, **64**, 497
[54] Childers, N. F., Robles, P. S. and Loustalot, A. J., Puerto Rico Fed. exp. Sta. Circ., 1948, 30
[55] Mirov, N. T., Wang, T. H. and Haagen-Smit, A. J., *J. Amer. pharm. Ass., Sci. Ed.*, 1949, **38**, 403
[56] Mirov, N. T., Haagen-Smit, A. J., and Thurlow, J., *J. Amer. pharm. Ass., Sci. Ed.*, 1949, **38**, 407
[56a] Schorger, A. W., Forest Service Bulletin, Wash., 119, 1913
[57] Matei, I. and Cocea, E., *Bull. École Polytech. Jassy*, 1948, **3** (1), 416, through *Biol. Abs.*, 1949, **23**, 30127
[58] Carter, C. L. and Heazlewood, W. V., *J. Soc. chem. Ind.*, 1949, **68**, 34
[59] Calder, A. J. and Carter, C. L., ibid., 355
[60] Chilquist, V., Gilmour, R. and Jannke, P., *J. Amer. pharm. Ass., Sci. Ed.*, 1949, **38**, 204
[61] Schmid, H. and Karrer, P., *Helv. Chim. Acta*, 1948, **31**, 1017
[62] Idem, ibid., 1087
[63] Hickey, M. J., *J. org. Chem.*, 1948, **13**, 443
[64] Holland, Johnson and Sorrels, Bull. agr. mech. Coll., Texas, Engng. Exp. Sta. 107, 1948
[65] Naves, Y. R., *Perf. essent. Oil Rec.*, 1949, **40**, 40
[66] Benezet, L. and Igolen, G., *Amer. Perfum.*, 1949, **54**, 455
[67] Schmidt, H., *Chem. Ber.*, 1947, **80**, 538
[68] Naves, Y. R., *Perfum. essent. Oil Rec.*, 1949, **40**, 197
[69] Sorenson and Hougen, *Acta chem. scand.*, 1948, **2**, 447
[70] Brandt, C. W. and Ross, D. J., *J. chem. Soc.*, **1949**, 2778
[71] Szmant, H. H. and Halpern, A., *J. Amer. chem. Soc.*, 1949, **71** (3), 1133
[72] Halpern, A., *Amer. J. Pharm.*, 1949, **121** (1), 5
[73] Rao, P. R., *J. sci. industr. Res., India*, 1948, **7B**, 166
[74] Fuchs, L and Matzke, G., *Scientia Pharm.*, 1949, **17**, 1
[75] Maltby, J. G. and Primavesi, G. R., *Analyst*, 1949, **74**, 498
[76] Mori, D., *Chim. Industr.*, 1948, **59**, 160
[77] Fritzsche Bros. Inc., *Drug and Cosmetic Ind.*, 1949, **64**, 620
[78] Lepetit, H., *Trav. des Lab. de Mat. Med. Pharm. Galen. de la Faculté de Pharm. de Paris*, through *Perfum. essent. Oil Rec.*, 1949, **40**, 194
[79] Julien, J., ibid., 195
[79a] Janot and Mouton, *J. pharm. Chim.*, 1936, **23** (8), 547
[79b] Leonard and Smith, *Analyst*, 1898, **23**, 281
[80] Hoffmann, F. A. M., *Ann. Ass. quim. Brasil*, 1949, **7**, 200
[81] Maurel, A., *Chem. Anal.*, 1949, **31**, 31
[82] Salamon and Seaber, *Perfum. essent. Oil Rec.*, 1949, **40**, 47
[83] Littlejohn, W. R., ibid., 422
[84] Langenau, E. E., *J. Amer. pharm. Ass., sci. Ed.*, 1949, **38**, 261
[85] Variochem V. V. B. Schimmel, *Perfum. essent. Oil Rec.*, 1949, **40**, 239
[86] Taylor, A. McM., ibid., 135
[87] McKern, H. H. G. and Smith-White, S., *J. Aust. chem. Inst.*, 1948, **15**, 276

SUGARS

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ONE of the most important aspects of sugar affairs of the 1948–49 season is the amount of the world production of sugar, which is the greatest ever recorded, being about 32,000,000[1] tons. This exceeds the previous year's crop by about 2,700,000 tons; however, sugar in Great Britain is still in short supply and we naturally turn to our own beet sugar industry and to our sugar-producing colonies to remedy this shortage. The beet sugar production for 1948–49 is estimated at 566,968 tons and this shows a marked increase over the previous year, when only 429,160 tons were produced in this country. This low return is doubtless due to adverse growing conditions because 556,731 tons and 503,475 tons were produced in 1946–47 and 1945–46 respectively. Turning to cane sugar production in the Empire we find very significant increases in production figures here also: for example, Australia and Fiji have increased their production to 1,078,360 tons from 747,911 tons for 1947–48, Mauritius from 348,531 in 1947–48 to 395,067 tons in 1948–49. The British West Indies also have increased production significantly and the analysis shown in Table I is of interest.

Table I[2]

Cane sugar production in the British West Indies and British Guiana

	1945–6	1946–7	1947–8	1948–9	Preliminary estimates for 1949–50
	tons	tons	tons	tons	tons
Trinidad	109,602	110,069	115,941	159,032	156,200
Barbados	113,880	88,024	57,758	132,731	137,500
Jamaica	177,886	170,255	192,814	237,825	251,500
Antigua	26,023	22,736	12,174	18,000	28,000
St. Kitts	33,513	34,357	31,393	35,667	37,000
Other B.W.I.	5,950	6,164	12,494	11,200	11,950
British Guiana	172,051	165,148	172,991	184,690	200,877
Total	638,905	596,753	595,565	779,145	823,027

Cuba, on the other hand, has decreased its production in 1948–49 by over 800,000 tons (i.e. 5,959,775 in 1947–48 to 5,145,644 in 1948–49) probably because of over-production (so far as concerns the American market) in the previous year.

These figures indicate that in general there is a fairly rapid upward trend in the sugar production of the world and surpluses may well occur in several countries during the next few years. Both the Sugar Research Foundation in America and the Colonial Products Research Council are

aware of this possibility because both organizations sponsor research on the utilization of sucrose as a chemical and in other ways.

An increase in the production of sucrose does, however, involve another problem, namely the utilization of the by-products of the sugar industry which will also be produced on a greater scale. With the beet industry there is no real problem, since the main by-product, the beet pulp, when dried and mixed with molasses forms an excellent cattle food. In the cane sugar industry, on the other hand, the efficient utilization of the two main by-products, bagasse and molasses, does constitute a difficulty. Bagasse is generally burnt as factory fuel but when better heat efficiency is introduced into the older factories and new factories are constructed, more than sufficient for this purpose will become available and this extra amount of bagasse will become an embarrassment to the factory. Molasses has from time to time in the history of the sugar industry been difficult to dispose of and with increased production of sugar this problem will assume a more serious character. The British West Indies form an example of this problem; during the past few years practically all of the molasses produced has been converted into rum, but this market is rapidly becoming saturated and molasses will have to be used for other purposes or be written off as a total loss to the sugar factory. Molasses is, however, a valuable source of carbohydrate materials and may be converted into many different products such as industrial alcohol, acetone and butanol, glycerol, lactic acid or levulinic acid; it appears to be a problem of some urgency for the prosperity of the British West Indies to develop the manufacture of such products at the sugar factories or other centres located in the Caribbean area. This question of the utilization of cane sugar and its by-products has been reviewed recently by the author of this report.[3,4]

The cane sugar industry

Agriculture

Since the discovery by Sir John Harrison and Bovell in 1888 that the sugar cane could be propagated by seed, great progress in the production of new varieties of cane has been made in several parts of the world. For example, Harrison developed new varieties in British Guiana to such an extent that by 1918 practically all of the old Bourbon canes had been replaced by new seedling varieties. The central cane-breeding station for the British Caribbean area is now situated at Barbados and this station has produced many new seedling canes that are now in commercial production in the West Indies. A summary of the modern work of the station was recently given by de L. Inniss.[5] In this article the author enumerated the outstanding seedlings produced in Barbados and emphasized that, whereas one particular variety of cane might grow well in one locality, it might fail or be susceptible to disease such as mosaic virus disease in another; for example, B.37,172 is fairly exacting in its ecological requirements and although excellent yields of cane are obtained in Trinidad, it does not relish the calcareous soil of Barbados or Antigua.

Considerable progress has been made in recent years in the sphere of sugar cane agronomy. Improved methods of cultivation giving an optimum tilth to the soil and the proper assay of fertilizer needs have

led to marked increases in yields of cane per acre. An account of one new system of cultivation emanating from Trinidad, namely the Woodford Lodge system, is given by Cahusac.[6] The essentials of this are cambered beds 24 ft. wide and cultivation in the dry season by knifing the subsoil to a depth of 18 in. and ploughing to 12 in. Turner[7] provides details of cultivation for the four main soil types in Jamaica.

Some increase in the degree of mechanization of sugar cane agriculture has been apparent in recent years, owing, no doubt, both to labour difficulties and high labour costs. Descriptions of new pieces of machinery designed especially for sugar cane agriculture have recently appeared.[8] Mechanization has probably taken place to the greatest extent in Hawaii but in the British West Indies considerable progress in this direction has also been made. Information as to the use of machines in cane cultivation has recently been provided in a publication of the Caribbean Commission.[9] Labour difficulties have also emphasized the problem of weed control and eradication, and extensive use is now being made of organic chemicals of the hormone and herbicide type. Stevenson[10] has recently described work done with 'Agroxone' (sodium 2-methyl-4-chlorophenoxyacetate) in British Guiana. This substance was found to eradicate efficiently the broad-leaved weed, wild eddo, particularly when used with soap solution, but to be less effective against the pernicious nut grass. Barnes[11] has indicated the use of such substances as 2 : 4-dichlorophenoxyacetic acid and its derivatives in Jamaica. A warning note was sounded, however, by N. S. Hansen[12] who suggests that the wide use of plant hormones and herbicides may have a deleterious effect on soil fertility because of their possible effect on soil micro-organisms.

The experience of Mauritius[13] in respect to the disease known as 'smut,' caused by the fungus *Ustilago sutaminea*, is of interest. It has been found that the main variety grown in that island, namely M.134/32, is relatively immune, but the disease may become epidemic in low-lying regions. Moreover, with susceptible varieties such as B.H.10/12 or White Tanna there is a seasonal variation in the fungal attack. In South Africa 'Bexadust' (a dust containing 0·5% gammexane) was found effective in the control of elegant grasshopper (*Zanoceras elegans*).[14] Dynastid beetles which attack the buds of planted cane cuttings were also controlled by this preparation or by DDT. In Australia[15] the greyback cane beetle, which attacks several varieties of cane, can be controlled by gammexane diluted with rock phosphate dust. White grub, wireworm, leaf scald and gumming disease are all controllable either by the use of insecticides or by the cultivation of resistant varieties. An informative account of the biological control of insect pests of sugar cane in the West Indies has been written by Simmonds,[16] who refers particularly to the small moth borer which spoils an appreciable amount of cane in the West Indies. The most important species is *Diatraea saccharalis*. In the northern islands such as Antigua this is controlled by a parasite, *Lixophaga diatraea*. In Barbados, the incidence of the moth borer has been reduced by the liberation of the egg parasite, *Trichogramma*. However, the problem of keeping down moth-borer infestation is still important in other areas because it seems that the well-known parasites cannot be established in those areas and research on the

effect of the liberation of new parasites is still needed. In Trinidad the froghopper, *Tomaspis saccharina* Dist., is a more serious pest which is difficult to control but there are indications that new organic ovicides will be very helpful in this problem.

Mosaic virus disease is a potential danger to sugar cane in many parts of the world and an important aspect of cane breeding is the resistance of the new seedlings to this disease. In Jamaica, the main variety grown, B.34/104, is fortunately tolerant to the virus of mosaic disease but the sugar industry there is always aware of the dangers of this disease because, if it did spring up, its effect could be devastating. Mosaic disease was the cause of the decline of the Louisiana cane sugar industry in the middle twenties; the industry revived because of the introduction of resistant varieties. Several different strains of the virus have been distinguished and there seems to be a varietal reaction to the different strains. Of the many hosts of the virus, *Zea mais* is particularly dangerous in Louisiana because it enters into the common rotation there and thus provides a source of infection, being host to the major vector of mosaic, *Aphis maidis*.

Sugar manufacture

So far as the British Caribbean area is concerned the past year has been one of some importance in the field of sugar manufacture because two large new factories have been completed, one at Monymusk in Jamaica and the other at Uitvlugt in British Guiana. Both have been built to operate on the conventional raw sugar process. The British Guiana factory, however, has made use of compressed air to a far greater extent than is usual so that reliance on gravity for the transport of the products of the various stages of the sugar process has been obviated and it has been possible to arrange the various stations of the factory so as to effect better supervision of the operations.

In discussing advances made in the manufacture of sugar during the year it will be advantageous to consider each station of the factory in turn, i.e. milling, clarification, subsidation and filtration, evaporation, crystallization and sugar curing; afterwards, the by-products of the industry can be considered.

Milling

Linlay[18] presented an interesting paper which was concerned with the pressure developed between the rollers of a sugar cane mill and he attempted to modify the known methods of calculation of that pressure. Schnuck[19] described certain modifications in a mill for controlling the flow of cane juice around the ends of the rollers in order to prevent its deleterious action on the working surfaces associated with the journals. The material constitution of the cane mill rollers is discussed by Hewitt[20] who points out that they should have a fairly tough iron surface with a coarse structure wearing to a rough grain which would grip the fibre passing through. Since a high carbon content is necessary to produce coarse graphitic flakes, a small amount of manganese (2%) is often used to give a stronger matrix structure. According to Gonzalez Mais[21] the use of machine-cut instead of cast steel gears for the mills and improved

velocity differential resulted in a better performance in some Cuban mills. The installation of sheet copper beds to several sugar mills in Cuba is also described; this is a great protection against bacterial infection of the juice and is also a security against leakage. It is quite certain that considerable losses are incurred in some cane sugar factories owing to the mills not being kept clean. If the area around the mills is not cleaned spilled juice is a breeding ground for micro-organisms and a source of contamination throughout the factory. Salinas of Cuba[22] advocates the use of a sanitary squad to spray around the mills with a suitable chlorine preparation ; ultra-violet light lamps placed in suitable positions are also of possible use.[23] The occurrence of fermentation at the grinding station will result in a high glucose ratio in the invert sugar present in the juice and hence cause greater molasses formation. Therefore, according to Gonzalez Mais, there is every reason to keep down the bacterial count of the juice at the mills by cleanliness and by the use of antibacterial preparations such as the Daniel chlorine process, which provides an antiseptic but does not increase the salt content of the juice.

Defecation: clarification

The defecation of cane juice is carried out by treatment with lime and the precise method of treatment has been varied in many ways. An interesting liming device making use of the ancient Chinese pumping wheel, together with a weir overflow, and a system of pivoted channels was described by Wright.[24] The weir was fed from a receiving trough and the surplus lime returned to the main tank in which the wheel revolved at about 5 r.p.m. The liming process, followed by heat treatment, serves to coagulate colloids present in the juice, to precipitate them, and to occlude others on a precipitate of calcium phosphate which necessarily forms because cane juice always contains a certain amount of phosphate ions. The colloids removed have been described as protein, waxy and fatty in nature, but the author considers the latter two materials to be the major constituents of cane juice colloids. The efficient removal of these colloids is, however, the crux of the sugar manufacturing process and on the efficiency of this operation will depend both the quality and amount of sugar obtained. In general practice successful clarification depends on the formation of a rapid-settling precipitate occluding the colloidal impurities in the juice. Salinas[22] emphasizes the importance to successful clarification of the ratio phosphoric oxide : total non-sugars in the juice—the clarification index—and he suggests that the index should have a value of not less than 10. The attainment of the necessary phosphate concentration is best achieved by correct application of fertilizer during cultivation of the cane. Salinas declares that phosphate naturally present in the juice is more effective for clarification purposes than phosphate added afterwards. With a fertilizer application of 600 lb. per acre of nitrogen, phosphorus and potassium in the ratio of 3 : 3 : 1, the juice from any variety of cane is said to clarify properly, provided that the cane has received a well distributed rainfall of about 60 in. Salinas also defines the temperature to which the limed juice should be heated as between 105 and 110° c. and the rate of passage through the juice heaters as not less than 6 ft. per sec. It is well known

that the juices of certain varieties of cane are more difficult to clarify than others and that climatic conditions also play a part in the efficiency of clarification; prolonged drought in Barbados during the 1948 crop produced juices that were extremely difficult to clarify. Observations have also been recorded on clarification difficulties associated with juices derived from diseased canes. Such juices contain more colloidal matter and more invert sugar than juice from healthy canes.[25] Leake[26] emphasizes the importance of using fresh canes in order to avoid clarification difficulties but the indication has been given that the addition of soda ash with the lime is the best way to counteract the rising acidity of juice from old canes.[27] Balch and Broeg[28] have shown that both burnt and unburnt cane deteriorates very rapidly particularly when wet; the presence of excess moisture increases the rate of growth of micro-organisms.

Deerr[29] and Toh Liu[30] demonstrated that asbestos is capable of precipitating colloids from solution. More recently clays such as bentonite have come into prominence, and Silva[31] describes the use of this material in some detail; bentonite is a hydrated aluminium silicate possessing marked base-exchanging and colloidal properties. It is applied to raw juice immediately before the liming stage in the form of a colloidal suspension at the rate of about 1 lb. per ton of cane. The process is then carried out in the usual manner except that the temperature in the juice heaters need be only 200° F. instead of the usual 212–220°. The purity of the clarified juice is raised at least 1% higher than that obtained by the usual process, scaling of the evaporators is reduced, less molasses is formed and the process seems to offer pronounced advantages; however, it may well be that the particular variety of cane used will affect the success of the process. Another clarification process of some promise is that devised by Naugle and Wickenden.[32] This makes use of a substance named Elguanite which consists principally of magnesium oxide and is used instead of lime; it is said to effect an excellent clarification and moreover its use does not involve heating the juice to a temperature higher than 85° C. Although little has been published about this procedure it would seem to be of considerable interest. A quite different method of clarification has been suggested by Ghosh[33]: this comprises the electrical coagulation of cane juice colloids by passing the juice over iron sheets attached to a supply of direct current. Another possible way of clarifying juice is by the use of high-speed centrifugal machines, through which the juice may be passed either before or after the liming stage. A patent describing a particular procedure has recently been published,[34] which consists in thickening the juice in an evaporator, centrifuging and finally concentrating to grain; the liquor may also be limed and treated with carbon dioxide before centrifuging. It is claimed that either procedure effects economies over the normal operations.

In the normal sugar factory the juice is limed and heated, and then the muds are allowed to settle either in intermittent or continuous subsiders, which are often of the Bach or Dorr designs; improvements in their working in a cane sugar factory have been described in the patent literature by Warren and Jordan.[35] The method used is to add lime to the hot juice in the clarifier at such a rate as to maintain the p_H at 7–8. To

do this milk of lime is added continuously into the mud blanket in the clarifier in order to raise the p_H of the mud and so prevent inversion of the sugar trapped therein. Further improvements to the Dorr type of clarifier were introduced by Geissler[36] who designed equipment capable of dealing separately with two products, for example primary and secondary juice from sugar cane. An important patent disclosure by Bollaert and Halvorsen describes a method of clarification involving the addition of lime under pressure at several points along the path of flow of a stream of juice already containing a filter aid such as diatomaceous earth and some phosphoric acid. It is claimed that this procedure results in the formation of a readily filterable precipitate and a better coloured clarified juice. Another procedure for clarification has been patented by Green, McBride and Hertzing.[38] In this the juice is clarified by mixing it in continuous flow with previously partly clarified juice, lime being added further along the circulating system. The mixture is then taken to a continuous clarifier where the heavy muds are removed; the juice passes upwards and a less clear portion is returned to the system and is mixed with fresh juice, the clear juice being sent on to the next stage of the sugar process. The idea of adding calcium carbonate to the juice in the clarifier as a means of settling the lighter floc in the ordinary sugar process is not new but the addition of this reagent in the form of ground oyster shells has recently been described as particularly efficacious in this respect.[39] Attempts to lessen sugar losses in a Bach subsider during stoppages have been described by Bullen,[40] who estimated that at a working temperature of 205° F. the sucrose loss in the subsider amounted to 1·53 tons for an overnight stoppage and 4·57 tons for a week-end stoppage. The best improvement that could be effected was to work at 190° F. and to pump out a portion of the mud at the time of the shut-down when losses are reduced to 0·65 tons over the week-end.

Ion-exchange resins

Ion-exchange resins cannot yet be said to have had any widespread use in cane sugar factories for increasing the purity of cane juice. There are two main objections: one is the high capital outlay involved, together with the high cost of regenerating the resins, and the second is the fact that there is a distinct danger of inverting some of the sucrose during the process. On the other hand, purity increases of more than 5% have been recorded and the elimination of scaling of evaporators would result from the use of an ion-exchange process; molasses formation would certainly be reduced and better quality sugar obtained. Mindler[41,42] has conducted a thorough investigation, using Cuban and Louisiana juices. He records that 90–95% of the ash and 70–75% of the non-sugars were removed from the juice; the purity rise for Cuban juice was 4·7% and for that from Louisiana, 6·5%; the yield of sugar was increased by 3·8% and 6·2% respectively. The process comprises the main defecation of juice with lime, the cooling of the resulting clarified juice to about 30° C. followed by its successive passage through the cation- and anion-exchange resins. It is practically certain, however, that residual colloids left in the clarified juice would soon reduce the efficiency of ion-exchange and it would seem that some sort of pre-filtration would be necessary. The

resin beds require rather special treatment for regeneration. Blann[43] describes a process in which 10% hydrochloric or sulphuric acid is applied to the anion-exchange resins before the usual alkali treatment in order to remove the colouring matter originally present in the cane juice from the surface of the resin particles. Several patents have been granted recently for cane juice purification by ion-exchange resins[44,45,46,47] and one to Campbell[48] describes a particular cation-exchange cell for the purification of sugar solutions, designed so that the solution is kept for the minimum time in contact with the resin bed. Meijer[49] describes in detail the preparation of a synthetic-resin gel claimed to remove organic impurities such as colouring matters and objectionably tasting and smelling compounds from sugar solution or from molasses; this is to be used after passing clarified juice over a cation-exchange resin and before treatment with an anion-exchange resin.

An interesting account of factory-scale studies on the use of ion-exchange purification has been written by Ellison and Porter,[50] who describe work done at the factory of the Layton Sugar Co., Utah. Relatively pure juice obtained after two carbonation treatments was the raw material: this was passed through six heat exchangers whereby it was cooled to 60–65° F. and then through four ion-exchange units; the purity of the juice was raised from 93·76 to 98·6 and the amount of invert sugar was only increased by 0·26%. It was necessary, however, to add small amounts of alkali to the evaporators from time to time to prevent the development of acidity owing to the unbuffered state of the deionized juice. It was recorded that an extraction of 92·03% was obtained compared with the 85% to be expected with normal sugar factory practice. An interesting observation was made during this work: although the juice entering the resin beds was quite heavily contaminated with micro-organisms, a considerable diminution in their concentration was observed in the effluent juice.

Dymond,[51] in discussing ion-exchange purification of cane juice in Natal, emphasizes the importance of pre-clarification treatment. One such procedure involves the addition of phosphoric acid to the juice to produce 0·03% phosphoric acid therein, followed by treatment with sulphur dioxide until the p_H falls to 3·2. Clay is then added (3·5–8 lb. per ton cane) to precipitate wax, gums, proteins etc., and the juice is filtered with the aid of 0·5% 'Hyflosupercel'; it is then passed through the resin beds. This process has an advantage over the usual lime–heat clarification because it is carried out in the cold. Moreover, it is also known that a much greater precipitation of colloids occurs under acid than under alkaline conditions (*see* Farnell[52]).

Two important advances in the preparation of synthetic resins of use in the purification of sugar juices have been made recently. One is the production of two new Amberlite resins IRA 400 and IRC 50.[53] IRA 400 will absorb negatively-charged ions from solutions of p_H 1–10; it possesses an exchange rate far greater than any other resins so far discovered. IRC 50 adsorbs cations and completes the deionization process. The use of these two resins in sugar juice purification has the advantage that at no stage is the juice at an acid p_H, so that both sucrose inversion and plant corrosion are eliminated. The second advance arises from the

first because the two new resins can be used in admixture and hence single-column sugar juice deionization becomes possible. Differences in density of the two resins makes it possible to isolate them by flotation and to regenerate them separately.[54,55] It remains to be seen what use the sugar industry will make of these inventions.

Filtration

The filter station of the majority of raw-sugar factories employs the Oliver–Campbell rotary vacuum filter. This equipment is much cleaner to work with than plate and frame presses and involves the use of much less labour; moreover, a much smaller sugar loss is incurred in the filter cake from these filters than in that from filter presses. The advantages and disadvantages of the Oliver filter are summarized by d'Avice[56] who refers especially to the use of this equipment in South Africa. The Oliver filter employs fine bagasse (bagacillo) as a filter aid. Whalley[57] declares that it should be of the fineness range 85–472 on Behne's scale; he also describes a pneumatic apparatus for providing such fine bagacillo. Compain[58] emphasizes the difficulties that are due to the filter often being located at a considerable distance from the source of the bagacillo, which has to be blown by hot air through long air ducts to be mixed with mud at the filter station. This author suggests that it might be better and more economical to transport the mud to the bagacillo source and then pump the mixture through a 4-in. pipe line to the filter station. A difficulty which sometimes occurs in using the Oliver filter is in the blocking of the holes of the copper screens with filter mud and a crystalline material which appears to be calcium oxalate; this is particularly difficult to remove. McCleary[59] claims that a double treatment with acid (inhibited with molasses) and alkali effectively clears the screens.

Considerable amounts of coarser impurities can be removed from cane juice at the milling end of the sugar process by using vibrating screens, and numerous types are on the market. The use of a new type, the 'Selectro Vibrator' screen, has been described in Hawaii[60]; although this is no better than others in the amount of juice purification it effects, it has a considerably increased capacity.

In normal practice only the settled muds of the raw sugar factory are filtered, but the possibility of filtering the so-called clear decanted juice should not be overlooked. Such a process would be certain to remove much of the residual colloidal matter still in suspension and the removal of this would certainly increase the amount of sugar crystallized. New filters have been recently invented which might be used for this purpose either at the clear juice or at the syrup stage. The 'Copenhagen' filter has been described by Ostenfeld[61]; this is a pressure filter operating with wire screens and using diatomaceous earth as filter aid. The 'Niagara' filter[62] is a leaf type pressure filter consisting of a vertical cylindrical vessel. The filter frames are tubular in section and rectangular in shape and have metal filter screens. The filter operates at up to 65 lb./sq. in. and uses filter aids such as 'Hyflosupercel' or 'Dicalite.' These filters are fitted with an 'auto-sluice' device which allows for completely automatic cake removal, thus obviating the necessity to open the filter in order to sluice the cake from the leaves.[63] Although such filters are used

mainly in the manufacture of syrup and of white sugar, their use in the production of raw sugar is of possible advantage for the reasons outlined above.

Evaporation

No striking improvements have been effected in the evaporator and vacuum pan stations of the cane sugar factory in recent years. The Williame vacuum pan deserves some comment, however, because although clearly not perfected it offers the possibility of boiling sugar to grain continuously. A brief description of the apparatus and that of similar construction by Werkspoor has been given recently.[64] The chief difficulty at the evaporator station lies in the scaling of the tubes. Numerous chemicals have been used as scale inhibitors such as tetraphosphoglucosate and Wricorg C, but no general appreciation of these has been forthcoming. Romero[65] describes the successful use of the former in Cuba but trials in the British West Indies have not given much success; 'Wricorg C' has also been examined in factories in Trinidad[66,67] and Barbados[68] but had no marked effect in decreasing evaporator scale in either place. Electrical appliances are now being marketed and hold out most hope of success. Two such devices are the C.E.P.I. anti-scaling device[69] and the Superstat[70] device; both are being tested thoroughly in raw sugar factories. The best remedy, however, is to eliminate the scale-forming salts altogether before they reach the evaporator. This can, of course, be done by means of ion-exchange resins, and the saving on this score should therefore be included in the cost estimates of the use of ion-exchange processes in raw sugar factories.

An interesting observation has been made by Suzuki[71] who finds that the presence of traces of manganese sulphate (0·001–0·003%) in sugar juice hastens its evaporation, probably by virtue of the fact that it decreases the viscosity of the syrup; it is also claimed that the presence of manganese salts reduces the rate of inversion of sucrose. A novel process for sugar evaporation is described in a Dutch patent[72]: this involves neutralizing the sugar juice with lime and then evaporating the mixture without settling or filtering; the thick juice is then subjected to carbonatation. It is claimed that no incrustation of the evaporator tubes occurs and that inversion of sucrose during evaporation is avoided. An idea to increase the capacity of the evaporators in a sugar factory has been put forward by Freeland[73] who advocates the use of an additional juice heater between the clarifiers and the evaporators. The evaporator station layout in Peru's new factory at 'Casa Grande' is of interest and consists of nine Kestner evaporators, two quadruple effects and one spare body; the details have been given by Tromp.[74]

An improved design of the Webre mechanical circulator for vacuum pans has been described by the inventor.[75] As well as describing the technical details of the improved circulator, the author reviews the advantages attached to its use in pan boiling. One particular advantage is the production of a uniform temperature throughout the massecuite and the avoidance of localized excessive heating. This would certainly decrease the decomposition of invert sugar by heat, a process which is known to increase the acidity of sugar solutions. Heat decomposition

of sugars must play a part in sugar manufacture; it is even possible to destroy the sucrose molecule completely by the action of water and heat alone provided the temperature is high enough.[76] An informative article on the Webre three-massecuite system with molasses graining, as used at the Central Mercedes factory in Cuba, has been contributed by Gonzalez.[77] This author demonstrates that this system has distinct advantages over the four-massecuite system previously used at Central Mercedes.

Crystallization and curing

With regard to the crystallization section of the factory two new designs of crystallizer have been described. One, patented by Dehn,[78] incorporates a rotary drum supporting heat exchange members and the second, the 'Acme' crystallizer, incorporates two oppositely directed helical coils mounted on opposite sides of the centre bearing; while these slowly revolve the crystallizing magma is brought into contact with all parts of the cooling surface. The movement also seems to spread seed crystals rapidly throughout the mass, producing crystals of even texture.[79] An article has also appeared describing the use of the Blanchard crystallizer.[80] The production in the crystallizer of false grains which clog the centrifugals is often a difficulty. Yarmolinskii[81] advocates spraying with hot water the low-grade massecuites discharging from the vacuum pan to the crystallizers, in order to dissolve the false grains; an automatic device is described. The results of physical chemical research on the rate of crystallization of sugar have been published in two papers.[82,83]

Few raw sugar factories have high-speed automatic centrifuges for the curing station but factories recently constructed are embodying this improvement, for example the new factory at Uitvlugt, British Guiana. Several such machines are in operation in South Africa[84] and are said to be responsible for reducing costs. The various electrical drive mechanisms used for centrifugal machines have been described by Grove[85] from the point of view of refinery practice. Some interesting observations on the shape and size of the holes in the screens for low grade sugar centrifugals have been reported from Australia.[86] It was found that the use of the normal-sized screens caused serious losses of low-grade sugars. A new screen having 600 holes (0·7 mm.) per sq. in. was used with success. More recent tests with fine stainless steel gauzes (90 mesh) soldered to the inner surface of the normal centrifuge screen showed further improvements.

An important aspect of sugar curing is the proper temperature control of the magma immediately before centrifuging; this has been achieved by passing the massecuite through a tank, arranged above the centrifugals, in which a coil heater was placed so that the massecuite could be maintained at the desired temperature. The Stevens mixer consists of a storage chamber below which is a heater compartment containing a rotating heating coil warmed with water, with thermostatic control of the massecuite temperature; the use of this device in Hawaii has recently been described by Hughes.[87] Hessey and Manning[88] have recently studied the effect of magma purity on centrifugal performance and have come to the conclusion that there is no need to use purities as high a

90 for the low grade massecuites; in fact the time of the centrifugal cycle is made unduly long, and magma purities of nearer 80 are advocated for speeding up low-grade sugar curing-time. Knox[89] made the interesting observation that the spraying of 2–3 l. of molasses, lasting for a few seconds, on to the low-grade sugar cake in the centrifuge while it was at maximum speed, improved the purity of the sugar from 83·05 to 83·9.

Shipment of sugar

A difficulty is likely to occur in future with regard to the transport of raw sugar because of the mounting costs of jute bags (in Australia the cost amounts to £2 per ton of sugar) and particular interest must be attached to a recent experimental bulk shipment of raw sugar.[90] This experiment was conducted in April 1949 when 5122 tons of sugar were transported from La Romana in the Dominican Republic to London. The sugar was 97·5° pol and contained 0·72% invert sugar and 0·73% moisture. It was placed in the ship's holds, which were specially cleaned and spread with tarpaulins, and at the start of the journey it was at 90° F. The sugar formed a hard crust but beneath this it kept in perfect condition. Bad weather caused a seepage of sea water into one hold and some of the sugar, 50 tons, was thereby damaged. The unloading of the cargo was carried out by means of mechanical grabs. These worked easily through the first 3 to 4 ft. of sugar but found the packed sugar beneath harder to deal with. The sugar was transferred to lighters and thence to silos situated at the refinery. Grabs were used to remove the sugar from the barges also. The experiment was considered a clear demonstration of the possibilities of the bulk shipping of sugar. Special machinery would be needed at the ports concerned if bulk shipment of sugar were carried out on a large scale; special conditions of work would also have to be elaborated for the labour involved.

By-products of the cane sugar industry

The main by-products of the industry are filter cake, bagasse and molasses; these will be considered in turn below.

Filter cake

Sugar factories now use filter cake on the land as a fertilizer rich in nitrogen and phosphate. However, it contains considerable quantities of wax, the amount of which is dependent on the particular variety of cane ground and probably on the climatic conditions during growth. In the British West Indies a Barbados cane, B.37.161, appears to be particularly rich in wax and filter cake (from Oliver filters) obtained from St. Kitts where this cane is extensively grown contains as much as 18% of the wax on a dry basis.[91] Since there is a pronounced shortage of waxes and the majority of these originate from hard currency areas, there is every reason for isolating this material from filter cake before using it on the land. Considerable quantities of wax are available in the British Caribbean area; it has been estimated that if there was an average wax content of 12% on filter cake, then some 7000 tons of crude wax could be produced annually.[92] Such a wax recovery process was carried out in South Africa from 1916–28 and has recently been started in Louisiana

and in Australia. The wax can be extracted from the dried filter cake with such solvents as benzene or petroleum hydrocarbons although the former seems to be the most efficient.[92] An informative article has been contributed by Shearer[93] dealing with the Australian work; the filter cake is dried to 18% moisture, coarsely ground and then extracted with Shell solvents X2, X3 or benzene. The crude wax is de-ashed by heating with diluted hydrochloric acid, washing out the acid with hot water. The wax is then melted to remove water which is drawn off, and the wax is run into moulds. Soft fatty materials are removed from the wax by re-crystallizing it from solvent X3 and acetone (the wax could be bleached by treating it with potassium chlorate in sulphuric acid solution at the boiling point and at the same time passing air through the emulsion). The chemicals are washed out and the wax melted and moulded. Shearer describes the plant used in all these operations.

Venton[94] also describes wax extraction in Australia; large differences in the wax content (3·6–18·5%) of filter cake from various areas are observed and it is suggested that this is due partly to the particular variety of cane being ground, partly to the clarification procedure being used, and partly to harvesting and milling methods. A continuous plant for wax extraction dealing with 1600 lb. cake per hour is described.

The two main problems in the purification of sugar cane wax are (i) its separation from soft fatty material and (ii) its decolorization. Crystallization would appear to be the best method of carrying out (i) and this may be done from such solvents as benzene itself, benzene–acetone or Shell X3–acetone. Alternatively cold pre-extraction of the fatty material with petroleum hydrocarbons, such as heptane, is effective;[95] this is followed by wax extraction with hot heptane. Another procedure was devised by Goepfert[96] in which the filter cake is extracted with hot *iso*propyl acetate; the extract is cooled and the precipitated crystalline hard wax filtered; the soft fatty matter remains dissolved in the *iso*propyl acetate.

A method of removing the resinous part of crude sugar cane wax was disclosed in a patent by Wilder.[97] This was accomplished by heating the wax with propyl alcohol; the resinous moiety is left undissolved and may be removed by decantation or filtration. On cooling the filtrate the hard wax separates and any soft material is left in solution. Another procedure has been patented by Svenson.[98] This consists in treating the hard wax with ketonic solvents or aliphatic hydrocarbons at such a temperature and pressure that the resinous fraction remains undissolved, and the wax proper passes into solution. The two layers formed may then be separated by decantation. A third refining process has been disclosed by Mcloud.[99] In this, sugar cane wax is heated with methanol at 95° C. under pressure, when the true wax dissolves and the resinous matter separates as a lower layer.

Bagasse

This is the conventional factory fuel of the raw sugar factory, but as improved furnaces are built and new methods of steam economy introduced an excess of bagasse is being obtained at a number of modern sugar factories and it is not uncommon to find large amounts of bagasse

being burnt merely to get rid of it. An interesting article on bagasse furnaces has recently been written by Gilg[100] in which the Ward furnace is described in detail. With modern improvements, excess bagasse is becoming an embarrassmnet to sugar factories and efficient and economical outlets are being sought. Since bagasse contains about 25% of pentosans it would appear to be a good source of furfuraldehyde and the production of this chemical may become of some importance to the sugar industry in the near future, particularly because of the added importance given to furfuraldehyde by modern research on its chemical behaviour.

Bagasse contains some 50% of cellulose and many attempts have therefore been made to manufacture paper from it but few have been successful. The Mestres process which is being operated at a factory at Santa Fé, Argentina, has however, been used there since 1943. It is noted that a factory for making fine paper and probably newsprint is being set up at Zatapec in Mexico : this will use bagasse cellulose mixed with about 20% of long-fibred bamboo pulp[101]. The calcium sulphite pulping process was investigated in Taiwan.[102] A yield of 42·4% of crude pulp was obtained which fell to 34·5% after bleaching with chlorine. This product contained 86·4% of α-cellulose, 7·4% of pentosans and 0·6% of lignin. A detailed analysis of bagasse and its ash has been made by De Almeida.[103] The preparation of an insulating board from bagasse termed Vazcane has previously been described by Vazquez[104] and this author has recently compared this with other board from bagasse and wood.[105] The same author[106] has described a process for making both cellulose and yeast from bagasse and has calculated that 3·5 tons of bagasse would yield 1 ton of cellulose and 0·5 ton of dried yeast. The process consists of the digestion of bagasse with 0·3% sulphuric acid at 135° C. for 1 hour ; the liquid is then expressed from the bagasse, neutralized with filter press cake and fermented with *Torula utilis*. The yeast thus made is used as a cattle food and the residue from the acid digestion as a source of cellulose. A review of the uses of bagasse was published by the Sugar Research Foundation in 1946[107] and has been brought up to date by Dr. Clarence West.[108]

Molasses

This is a by-product of the cane sugar industry and its disposal causes most trouble. It is produced in amounts varying from 700 to 800 lb. (about 50 gal.) per ton of raw sugar and therefore if it is not utilized quickly huge stocks would soon build up. In the British West Indies in recent years there has been no molasses disposal problem because practically all has been converted into rum. This market is, however, practically saturated and the old question of molasses disposal has loomed up again. It is not very likely that the shipping of molasses to this country would confer any great economic benefit to the colonies and so consideration must be given to its utilization at the site of production. Since molasses contains appreciable quantities of sucrose, it could provide an additional source of that commodity if it was found possible to recover the sucrose from it. The other constituents of molasses such as the melanoidins and other colloidal bodies, salts, glucose and fructose prevent the further crystallization of the sugar. Gonzalez Mais[109] declares that

glucose is in fact the principal melassigenic factor. The theory of molasses formation has also been discussed by Kaganov.[110] Efforts have therefore been made to purify molasses from these other materials in order to induce more sugar to crystallize. Reich[111] obtains the crystallization of a further amount of sucrose from molasses by treating it with an ammoniacal solution of ethyl and propyl alcohols (1 : 1). An extract of high sucrose concentration is obtained and from this 2 lb. of sucrose per gal. of molasses crystallizes. This work refers, however, to refinery molasses.

A process for the recovery of sucrose from cane molasses has been devised by Kloppenberg[112]. This depends on the fractional precipitation of the calcium derivatives of glucose and sucrose from alcoholic solution. Molasses is diluted with 3½ times its weight of alcohol, the precipitated gums and pectins are filtered off and the solution treated with powdered quicklime (1/6 to 1/7 of the weight of molasses) at 45–70° C. At this temperature the calcium derivative of glucose only is precipitated and is filtered off. The filtrate is treated with more lime, which causes the calcium derivative of sucrose to deposit; this can be used instead of lime in the sugar factory, or sugar may be recovered from it by decomposition with carbon dioxide, filtration and subsequent crystallization. Ginter and Manzoni[113] use barium hydroxide to precipitate the barium derivative of sucrose from molasses. Ion-exchange resins give a means of removing the salts from molasses and van Doormaal[114] claims that a 60–70% recovery of sugar in beet molasses may thereby be obtained.

Molasses also contains large amounts of potassium salts and an interesting method of recovery has been described by Mukherji.[115] Diluted molasses was treated with a solution of calcium dipicrylamine and the red precipitate of potassium dipicrylamine was filtered off; the recovery of potassium in this form was between 93 and 97% of the theoretical. Unfortunately, recovery of the expensive dipicrylamine could not be raised higher than 85%. Thus for recovery of potassium from 100 lb. molasses 50 lb. of reagent would be required, and for recovery of potash from a second batch of molasses an additional 7·5 lb. dipicrylamine would be required.

It is interesting to note that molasses contains appreciable quantities of *B* group vitamins[116], those present in largest amounts being nicotinic acid and pantothenic acid. Molasses also contains aconitic acid which is proving of considerable interest in the field of plastics. The content is very variable (1–5%) but it can be relatively easily recovered by using the low solubility of the calcium magnesium double salt. In the 1948 season 180 tons of aconitic acid were obtained during the production of a 190,000 ton crop of sugar.[117,118] In Louisiana the continuous separation of calcium magnesium aconitate from diluted molasses is carried out by means of specially designed De Laval Centrifugal machines.[119,120] A method of preparing calcium aconitate from the calcium magnesium double salt has been patented.[121] The process consists of heating the double salt with a solution of calcium chloride which furnishes soluble magnesium chloride and insoluble calcium aconitate. A process for obtaining essentially pure calcium aconitate directly from molasses has been disclosed by Ventre.[122] This involves heating diluted molasses

(28–30° Baumé) at 60° C. when part of the calcium aconitate precipitates and is removed by decantation. When calcium chloride and lime (to p_H 6·9) are added to the clear liquid at 60° C. the rest of the calcium aconitate separates. Evaporator scale also contains salts of aconitic acid and McGlashan[123] has described how the acid may be prepared from them.

The use of molasses in dry form as a cattle food has long been known; the mixture of molasses with bagasse, known as molascuit,[124] was exported from British Guiana in quite large quantities in the early part of this century and its use in this way has been advocated from time to time since. The use of molasses in powdered form in food preparations is possible in view of a patent describing a method, and the equipment, for drying molasses.[125] The process involves drying molasses as a film on revolving drums and storing the powder in sealed containers.

It has been claimed also that molasses is a good fertilizer for cane fields since it contains large amounts of nutrient salts including some 5% of potash. Shu[126] describes its use as such in Taiwan where about 10–15 tons per acre was applied in the case of new sugar land and 2–5 tons on established sugar land. It may be that the sugar in the molasses also plays a part in its fertilizing action as it would promote the growth of micro-organisms in the soil. The growth of moulds on the surface would lead to improvement in the moisture-retaining properties and the mycelium produced would increase the humus in the soil.

A considerable amount of work on the fermentation of molasses with various micro-organisms has been published during the year. Food yeast production is being carried on in a factory in Jamaica. Shukla[127] has described a concentrated nitrogen yeast-food rich in vitamins, prepared from final molasses by autolysing the yeast produced and concentrating the product in a vacuum pan. The value of the biotin in molasses in the production of baker's yeast has been emphasized in a paper read at the International Congress of Biochemistry.[128] Vacuum pan molasses was found to contain 1·1–1·6 μg. of biotin per g., beet molasses containing only 0·015–0·04 μg. A method of preparation of nucleotides from yeast has been patented.[129]

In a Russian patent[130] the production of citric acid from molasses is described and involves the building up of the organisms to withstand the non-sugar impurities in the molasses. Another patent describes the submerged fermentation of sugar with *Aspergillus niger* to give citric acid in 79% yield (on the sugar present). Further work on the fermentation of molasses to citric acid is recorded by Kovats[131] who provides data on the optimum p_H and temperature conditions for the fermentation. Full details of the procedure used in Germany for the production of citric acid from beet molasses have been provided in a report by officials of the Department of Trade and Commerce, Canada.[132]

Another carboxylic acid readily obtained from molasses is lactic acid. This is usually obtained by a fermentation process and observations on this have been recorded by Politi.[133] The production of calcium lactate from molasses by fermentation with *Lactobacillus delbruckii* is claimed to give an efficiency of 85% on the available sugar. It is to be noted however, that the fermentation required 8–14 days for completion. The

lactic acid, as it was produced, was neutralized with calcium carbonate and the product was finally isolated by centrifugal separation.[134] In addition to describing a fermentation process a recent article[135] indicates many uses to which lactic acid may be put; its main use, however, is doubtless in leather processing. Montgomery[136] has recently summarized knowledge on the production of this substance by chemical means. Haworth, Gregory and Wiggins[137] showed that yields as high as 71% of the theoretical of pure zinc lactate could be obtained by the action of lime on pure sucrose, and molasses could doubtless be used as a sugar source for this process. It is probable that if such a process were successful that new uses for lactic acid would be developed. A particularly interesting indication of this is the work of Fisher and his collaborators[138] on the conversion of lactic acid into acrylic acid and plastics derived from it.

Alcoholic fermentation of molasses.—It is noteworthy that a new distillery has been erected at Cuidad Trujillo in the Dominican Republic.[139] This is the largest in the West Indies having an initial capacity of 16,000 gal. daily. Some comments have been made recently [140] on the economic competition between fermentation and synthetic alcohol. The general conclusion reached was that fermentation alcohol is more expensive than synthetic alcohol made in existing plants but that the position would be reversed when new plant has to be erected because of the high costs obtaining today. Further, since in the fermentation method the price of molasses largely controls the position because the plant required is relatively simple, the recent fall in price of molasses will favour production of alcohol by this method.

An account [141] of the improvements in alcohol fermentation by the Melle-Boinot method shows that it effects a substantial reduction in manufacturing costs. The principle of this procedure is the repeated re-use of yeast cells in order to avoid the formation of new cells at the expense of sugar. The process involves the separation of yeast in De Laval centrifugal machines before distillation is effected and the return of the yeast to fresh fermentation mash. The fermentation times are 12 to 18 hours and yields of 9 to 10% of alcohol in the liquid are obtained. Reich[142] has also recorded some observations on his improved alcoholic fermentation process. In this a preliminary treatment of molasses with sulphuric acid precipitates lime salts which are removed. The fermentation is then carried out normally, but alcohol distillation and concentration of the stillage are carried out simultaneously. The stillage residue is carbonized and potash leached out and recovered. Carbon dioxide is recovered from the fermentation tanks and is purified and converted into dry ice. Perdomo[143] has attempted to find the optimum p_H at which alcoholic fermentation should be carried out. This was found to vary from sample to sample of molasses but was between 4 and 5. It was possible to obtain a fairly precise value for each batch of molasses used. A process for the continuous fermentation of molasses to alcohol has been patented by de Mattos[144]; it comprises passing the nutrient medium into a main zone of high yeast concentration, fermenting the sugars to alcohol and flowing the residue through zones of decreasing yeast concentration until a zone of high alcohol and low yeast concentration is

reached. Barneto[145] has made the observation that the addition of small amounts of pentachlorophenol to the fermenting mash eliminates bacterial contamination and leads to higher alcohol yields. Boinot[146] has observed the formation of sulphur dioxide during alcoholic fermentation and has found that it did not effect this, but caused corrosion in the plant. Its formation was avoided by adding more nutrient salts such as ammonium hydrogen phosphate.

A new rum distillery process has been described by Arroyo[147] in which rum of a predetermined quality, not requiring ageing, is produced. Neutral spirit (170–189 proof) is obtained from a continuous still and the high-boiling fractions collected and refractionated; portions of the fractions obtained are then blended with the neutral spirit to produce the required quality rum. The same author has contributed an informative article on rum distillery yields and the factors affecting them. The effect of the raw material on the flavour and aroma of rum has been studied by Guillaume[149] using Martinique rums. Rum distilled without removal of the lees has a more pronounced aroma. Molasses often deteriorates in storage even over a few weeks and Owen[150] has studied the fermentation characteristics of such molasses. He comes to the conclusion that efficient alcohol yields can be obtained from it if no nitrogen nutrient is added to the mash; that is, sufficient nitrogen for the yeast cells is already present in the deteriorated molasses.

The disposal of the dunder from distilleries is often a difficult matter owing to its objectionable odour; furthermore, useful products such as potassium salts are present in this material. A process has recently been described for spray-drying dunder so that the solids might be recovered from it.[151] Thaysen[152] reviews the whole subject of the disposal of dunder and advocates its use in making up the fermentation mash.

A number of interesting papers on the unfermentable reducing substances in molasses have been published in the past by Sattler and Zerban and several new additions to their publications have been made during the past year. In one,[153] they find that volatile constituents in the unfermentable residue from cane molasses contribute about 10% to its total reducing power. They identified acetol and methylglyoxal and also hydroxymethylfurfuraldehyde, levulinic acid, formic acid and acetoin. In a discussion on melanoidin formation they conclude that there are several types of melanoidins, some of which, although not fermented by yeast, produce fermentable sugars on acid hydrolysis and therefore must be formed from sugars. Erb and Zerban[154] determined in several molasses samples the unfermentable reducing sugars, the sucrose and the invert sugar content, and found it possible to predict alcohol yields fairly accurately. Zerban[155] has reported that the Java method for the determination of unfermentable reducing substances in molasses gives excellent results. Another paper[156] has been concerned with the nature of glutose, the unfermentable reducing substance obtained by heating a concentrated fructose solution, which de Bruyn and van Ekenstein believed to be a 3-ketohexose. It was found, however, that glutose is a mixture and contains acetol or methylglyoxal and acetoin as well as a substance which gives rise to glucosazone and several fructose anhydrides.

While considering fermentation processes it is noteworthy that methods for the production of dextran have recently been published in the patent literature. Owen[157] describes its production from a medium containing sugar or molasses, tryptophan, yeast extract and dipotassium hydrogen phosphate by growing *Leuconostoc mesenteroides* (Cienkowski) Van Tieghem in it, the dextran being precipitated by alcohol. Haworth and Stacey[158] describe its preparation using *Betacoccus arabinosaceus* (Birmingham) under aeration, again precipitating the dextran with alcohol.

Production of useful substances from sugar and the by-products of the sugar industry.—Several reviews on this subject have appeared recently. Wiggins has provided a broad review of the whole question[159] and also dealt with more specialized aspects such as the use of sugar itself as a chemical[160] and the use of sugar by-products.[161] Long[162] has dealt with sugar and sugar by-products in the plastics industry. Therefore no more need be said on this subject here.

Analysis of sugar and sugar by-products

De Whalley[163] describes a method of manufacture of pure sucrose for use in analysis. This sugar contains no more than 0·001% ash and 0·0015% organic non-sugars. Thus by difference, the sample contains 99·996% sucrose. Eynon and Lane[164] found that such sugar as this, made in a commercial refinery, is difficult to improve on and is adequate for analytical work. Gillett provides details of the conductimetic determination of ash in both raw and white sugar.[165] The relationship between ash and specific conductivity in the case of raw sugars is: per cent. resulphated ash = 0·0016 × specific conductivity (mhos); and for white sugars: per cent. ash = 0·00047 × specific conductivity (mhos). Estigneev has suggested that, since sucrose shows only weak absorption of light in the ultra-violet region of the spectrum and the impurities expected in it show considerable absorption with distinct maxima, the absorption spectrum of refined sugar should provide a method of quality evaluation.[166]

Englis and Miles[167] have worked out a colorimetric method for determining fructose in the presence of glucose. This depends on the fact that whereas fructose has a pronounced reducing action on the Folin–Denis phosphotungstate–phosphomolybdate reagent, glucose has only a slight action. Thus, the colour produced when a mixture of glucose and fructose is treated with the reagent under precisely controlled conditions, is due to fructose alone. The glucose in such a mixture may, of course, be found by determining total reducing sugars by another method and subtracting the amount of fructose found present by the molybdenum colour reaction. Stern and Kirk[168] have so improved the ferricyanide method of sugar analysis that sucrose and glucose in 1–8-μg. amounts may be determined to $\pm$ 2–3%. An electrometric procedure has also been reported for the determination of reducing sugars in macro quantities using potassium ferricyanide.[169] The preparation of a stable solution of invert sugar was described by Eynon and Lane at the recently held meeting of the British Committee of the International Commission for Uniform Methods of Sugar Analysis.[170] The procedure involves the use

of benzoic acid as an inhibitor of the growth of moulds and bacteria in the standard solution.

A new test for fructose has been devised by Whitehead and Bradbury.[171] In this, the sample in aqueous solution is treated with 3 : 5-dinitrosalicylic acid and sodium carbonate at 80–90° C. Sodium hydroxide is added to the cooled solution, and the presence of fructose is shown by the development of a red colour. The test is sensitive to 2 mg. fructose per c.c. of solution. The reaction of hexoses with cysteine hydrochloride and sulphuric acid has been developed by Dische *et al.*[172] into a spectrophotometric method of quantitative determination.

Ramanaiah and Narasingarao[173] show that errors in the determination of sucrose by Clerget are caused by the presence of excess de-leading agents such as sodium phosphate or potassium oxalate but that these are avoided by the use of potassium chromate, the amount of which can be controlled by spot testing with silver nitrate. Clarification with aluminium hydroxide also gives good results.

Hindin *et al.* [174] have found that the determination of invert sugar can be made spectrophotometrically by measuring unreduced copper in the solution after precipitated cuprous oxide has been centrifuged off. A polarographic method of determining fructose has been described by Vavruch[175] and this is capable of accurate use down to 10^{-5}M. concentration of the sugar. Zerban, Hughes and Nygren[176] have compared the determination of reducing sugar by the Lane and Eynon and the ferricyanide methods and conclude that the former is the best. Shaffer and Somogyi's method for reducing sugars has also recently been studied and improvements effected,[177] particularly from the point of view of yields of cuprous oxide obtained which have been raised by 10%. The reducing powers of 16 sugars were determined.

Considerable advances in the chromatography of sugars have been made recently. Binkley and Wolfrom's report[178] forms an excellent basis for study in this field. Jermyn and Isherwood[179] describe improved solvent mixtures, namely ethyl acetate–acetic acid–water and ethyl acetate–pyridine for use in the separation of sugars by paper partition chromatography. Hirst and Jones[180] have described a method of estimating sugars, separated on paper in μg.-quantities, by means of sodium periodate. The separation of larger amounts of sugars and their methylated derivatives by partition chromatography on columns of powdered cellulose has also been recorded, together with a description of an automatic receiver-changer for continuously collecting fractions from the column.[181] Two new spraying reagents for the paper chromatography of sugars have been reported. Partridge[182] has found that aniline hydrogen phthalate is an excellent reagent much superior to the silver nitrate reagent used hitherto; it gives different colours with pentoses and hexoses. Horrucks[183] has found benzidine in acetic acid–alcohol to be a useful reagent.

The advent of the high speed mixer such as the 'Turmix' and 'Atomix' has led to improvements in the procedures for the analysis of bagasse[184] and of beet cossettes and beet pulp.[185] In the case of bagasse the aqueous mixture is mixed for 10–15 min. when the temperature rises to 55° C.; it is filtered, the filtrate examined polarimetrically, and the residue

weighed as fibre. With beet cossettes only a 3-min. mixing time is required.

A very useful booklet on analytical procedures in use in raw sugar factories in Jamaica has been published by the Jamaican Association of Sugar Technologists.[186] Of some interest is the report that the Spreckels Sugar Co.[187] have developed a fully automatic polariscope which not only measures the optical activity of a sugar solution but prints its sugar content on a tare ticket.

It will be noted that the author of this review has not discussed, except in passing, the results of work specifically associated with the beet sugar industry or with sugar refinering, but has been mainly concerned with the cane sugar industry. It would not be fitting, however, to make no reference to the novel method of 'refining' sugar devised by Othmer.[188] In this process raw sugar is washed countercurrently in a screw conveyor with hot methanol, when a sugar of light-yellow colour is directly obtained of 99·7% polarization, the methanol being recovered by distillation. The residue from this is similar to refiner's syrup but is richer in vitamins. The process cannot however be regarded as being comparable with what is usually understood by sugar refining. The methanol treatment can only remove external impurities, that is mainly the molasses film. It cannot remove interstitial impurities in the crystals and it apparently does not produce a white sugar. Nevertheless, it is a very interesting process and may have possibilities of use in conjunction with the normal refining process or in producing special sugars.

References

1 The West India Committee Circular, November, 1949
2 Published by courtesy of the West India Committee
3 Wiggins, L. F., 'Advances in Carbohydrate Chemistry,' 1949, Vol. 4, 293
4 Idem, *Chem. & Ind.*, **1949**, 555
5 de L. Innis, B., Proc. Brit. West Indies Sugar Tech. Meeting, 1948, 28
6 Cahusac, H. C., *Jamaican Assoc. Sugar Technol. J.*, 1948, **11**, 80
7 Turner, P. E., ibid., 84
8 *Int. Sug. J.*, 1949, **51**, 12, 184
9 Caribbean Commission Crop Inquiry Series No. 6, Washington, D.C., 1947
10 Stevenson, G. C., Proc. Brit. West Indies Sugar Tech. Meeting, 1948, 62
11 Barnes, A. C., ibid., 74
12 Hansen, N. S., *Hawaiian Sug. Planters Record*, 1948, **52**, 113
13 Wiehe, P. O., *Rev. agric. L'Ile Maurice*, 1949, **28**, 7
14 *Int. Sug. J.*, 1949, **51**, 299
15 Ibid., 157
16 Simmonds, F. J., Proc. Brit. West Indies Sugar Tech. Meeting, 1948, 66
17 Summers, E. M., Brandes, E. W. and Rands, R. D., U.S. Dept. Agric. Tech. Bull. No. 9551, 1948, 124
18 Linlay, R. A., Proc. Brit. West Indies Sugar Tech. Meeting, 1948, 34
19 Schnuck, C. F., U.S.P. 2,448,195
20 Hewitt, W. V., *Int. Sug. J.*, 1948, **50**, 38
21 Gonzalez Mais, J. C., ibid., 1949, **51**, 87
22 Salinas, J. C., ibid., 87
23 Garcia, D. J. and Santa Marina, G., ibid., 228
24 Wright, F. B., ibid., 114
25 Khanna, K. L. and Chacravarti, A. S., *Curr. Sci.*, 1949, **18**, 19
26 Leake, F. B., *Sug. Bull.*, 1949, **27**, 382
27 Anon., ibid., 382

[28] Balch, R. T., and Broeg, C. B., *Sugar*, 1949, **44**, No. 6, 56
[29] Deerr, N., 'Cane Sugar,' 2nd Ed., p. 257
[30] Toh Liu., *Int. Sug. J.*, 1946, **48**, 262
[31] Silva, F. J. R., ibid., 1949, **51**, 85
[32] Naugle, J. S. and Wickenden, L., U.S.P., 2,441,281
[33] Ghosh, D. N., *J. Indian chem. Soc. industr. News Ed.*, 1948, **9**, 82
[34] Lindgren, H. O., U.S.P. 2,478,971
[35] Jordan, R. A. and Warren, G. T., U.S.P. 2,470,076
[36] Geissler, W. E., U.S.P. 2,377,875
[37] Bollaert, A. R. and Halvorsen, G. G., U.S.P. 2,470,332
[38] Green, W. H., McBride, G. A. and Hertzing, G. A., U.S.P. 2,458,261
[39] *The Sugar J.*, 1948–9, **11**, No. 8, 13
[40] Bullen, J., *Int. Sug. J.*, 1948, **50**, 261
[41] Mindler, A. B., *Ind. Eng. Chem.*, 1948, **40**, 1211
[42] Nachod, F. C. 'Ion Exchange Theory and Application,' 1949, (Academic Press Inc.)
[43] Blann, W. A., U.S.P. 2,451,272
[44] Rawlings, F. N., U.S.P. 2,391,843
[45] Dorr Co. Inc., B.P. 557,690
[46] Valley, H. A., U.S.P. 2,388,194
[47] American Cyanamide Co., B.P. 621,225
[48] Campbell, R. C., U.S.P. 2,458,893
[49] Meijer, H. W., B.P. 620,581
[50] Ellison, H. E. and Porter, L. B., *Sugar*, 1948, **43**, No. 3, 30
[51] Dymond, G. C., Proc. 22nd Ann. Congr. South African Sugar Technologists Assoc., 1948, 74
[52] Farnell, R. G. W., *Int. Sug. J.*, 1924, **26**, 420
[53] Willcox, O. W., *Sugar*, 1948, **43**, No. 12, 27
[54] *Int. Sug. J.*, 1949, **51**, 323
[55] 'Bulletin on Mixed Bed Deionisation,' Rohm & Haas Co., Philadelphia, 5, Pa.
[56] d'Avice, R., *Int. Sug. J.*, 1948, **50**, 295
[57] Whalley, T. G. *Proc. Queensland Soc. Sugar Cane Technol.*, 1949, **16**, 109
[58] Compain, J. D., *Int. Sug. J.*, 1949, **51**, 115
[59] McCleary, W. L., 67th Ann. Meeting Hawaiian Sugar Planters Ass., 1947, 87
[60] Idem, *Int. Sug. J.*, 1949, **51**, 227
[61] Ostenfeld, H. B., *Sugar*, 1948, **43**, No. 7, 24
[62] Ulrich, E. A., ibid., 1947, **41**, No. 4, 22
[63] Edrington, M. P. and Weinstein, S., ibid., 1948, **42**, No. 10, 35
[64] *Int. Sug. J.*, 1949, **51**, 27
[65] Pichardo, G. M. and Lima Romero, J. J., *Mem. asoc. technicos. azucar. Cuba*, 1948, **22**, 187
[66] Knox, P. J., Proc. Brit. West Indies Sugar Tech. Meeting, 1948, 87
[67] Schmidt, N. O., ibid., **1949** (in the press)
[68] Thorne, J. H. C., ibid.
[69] *Int. Sug. J.*, 1949, **51**, 343
[70] Bulletin on Electronic Water Treatment, Superstat Ltd., London
[71] Suzuki, K., *Int. Sug. J.*, 1949, **51**, 231
[72] Vereenigde Vorstenlandsche Cultuur-Maatschappij N.V., Netherlands Pat. 61,916.
[73] Freeland, E. C., *The Sugar J.*, 1949–50, **12**, No. 2, 10
[74] Tromp, L. A., *Int. Sug. J.*, 1949, **51**, 272
[75] Webre, A., ibid., 33
[76] Montgomery, R, and Wiggins, L. F., *J. Soc. chem. Ind.*, 1947, **66**, 31
[77] Gonzalez, S., *Int. Sug. J.*, 1949, **51**, 139
[78] Dehn, F. B., B.P. 598,052
[79] *Int. Sug. J.*, 1949, **51**, 95
[80] Fundora, G. and Rubio, A. R., ibid., 161
[81] Yarmolinskii, M. B., *Sakharnaya Prom.*, 1949, **23**, No. 5, 31
[82] Zhvirblyanskii, Y. M., Volobueva, A. K. and Abrogem, D. R., ibid., No. 1, 10
[83] van Hook, A., *Ind. Eng. Chem.*, 1949, **40**, 85
[84] d'Avice, R., *Revue agricole (Mauritius)*, 1949, **26**, 3
[85] Grove, P. F., *Int. Sug. J.*, 1949, **51**, 246

[86] Wright, *Proc. Queensland Soc. Sugar Cane Technol.*, 1948, **15**, 111
[87] Hughes, R. H., *Int. Sug. J.*, 1949, **51**, 77
[88] Hessey, R. W. G. and Manning, R. N., *Proc. Queensland Soc. Sugar Cane Technol.*, 1949, **16**, 87
[89] Knox, P. J., Proc. Brit. West Indies Sugar Tech. Meeting, 1948, 123
[90] Sudbury, F. A., *Int. Sug. J.*, 1949, **51**, 217
[91] Wiggins, L. F., Proc. Brit. West Indies Sugar Tech. Meeting, 1949 (in the press)
[92] Wiggins, L. F., *Chem. & Ind.*, **1949**, 555
[93] Shearer, A., *Int. Sug. J.*, 1949, **51**, 196
[94] Venton, C. B., ibid., 55
[95] Merz, V., Personal communication
[96] Goepfert, W. F., U.S.P. 2,430,012
[97] Wilder, F. A., U.S.P. 2,456,661
[98] Svensen, O. J., U.S.P. 2,464,189
[99] Mcloud, E. S., U.S.P. 2,456,641
[100] Gilg, F. X., *Int. Sug. J.*, 1949, **51**, 105
[101] Ibid., 191
[102] Hu, Y. and Chow, T. C., Report of Taiwan Sugar Experiment Station, 1947, No. 2, 29 ; *Int. Sug. J.*, 1949, **51**, 64
[103] De Almeida, S. R., *Brazil acucareiro*, 1948, **31**, 632
[104] Vazquez, E. A., *Int. Sug. J.*, 1948, **50**, 48
[105] Idem, ibid., 1949, **51**, 149
[106] Idem, *Bol. off. Asoc. Tecn. Azuc.*, 1948, **7**, 39
[107] West, C. J., Scientific Report series No. 3, Sugar Research Foundation (N.Y., 1946)
[108] West, C. J., Scientific Report Series No. 3 (supplement), Sugar Research Foundation (N.Y., 1949)
[109] Gonzalez Mais, J. C., *Sugar*, 1949, **44**, No. 2, 54
[110] Kaganov, L. N., *Sakharnaya Prom.*, 1948, **22**, No. 3, 21
[111] Reich, G., *Sugar*, 1949, **44**, No. 6, 32
[112] Kloppenberg, C. A., *Indian Sugar*, 1948, **11**, 285
[113] Ginter, H. and Manzoni, H., Belg. Pat., 474, 502
[114] Van Doormaal, J. J., 7th Congr. Internat. Ind. Agr., Paris, 1948, **1**, Q4–G
[115] Mukherji, B. K., *Int. Sug. J.*, 1949, **51**, 141
[116] Rogers, D. and Mickelson, M. N., *Ind. Eng. Chem.*, 1948, **40**, 527
[117] Furse, R. J. and Godchaux, L., *Int. Sug. J.*, 1949, **51**, 177
[118] Godchaux, L., *The Sugar J.*, 1948-9, **11**, No. 11, 3
[119] *Int. Sug. J.*, 1949, **51**, 236
[120] *De Laval Centrifugal Review*, 1949, **15** (1), 3, 11
[121] Ambler, J. A. and Roberts, E. J., U.S.P. 2,432,223
[122] Ventre, E. M., U.S.P. 2,469,090
[123] McGlashan, J., *Int. Sug. J.*, 1949, **51**, 31
[124] Bourne, C. A., *Ind. Eng. Chem.*, 1919, **11**, 876
[125] Stevens, A. H., B.P. 608,137
[126] Shu, K. H., *Taiwan Sugar J. Quart.*, 1949, **2** (2), 51
[127] Shukla, J. P., *Sugar*, 1949, **44**, No. 6, 57
[128] Dawson, E. R. and Harrison, J. S., 1st Int. Congr. Bioch., 1949, Abstr. of Comm., 546
[129] Schwarz Laboratories Inc., B.P. 615,891
[130] Kh. Val' dshstein, A., U.S.S.R. Pat. 69,300
[131] Kovats, J., *Gaz. Cukr.*, 1949, **89**, 30
[132] *Int. Sug. J.*, 1949, **51**, 300
[133] Politi, I., *Ann. Microbiol (Milan)*, 1943, **3**, 101 ; *Chem. Abstr.*, 1949, **43**, 6359
[134] Narula, B. L. and Chawla, B. R., *Indian Sugar*, 1948, **11**, No. 7, 115
[135] *Int. Sug. J.*, 1949, **51**, 203
[136] Montgomery, R., Scientific Report Series, No. 11, Sugar Research Foundation (N.Y., 1949)
[137] Haworth, Sir N., Gregory, H. and Wiggins, L. F., *J. Soc. chem. Ind.*, 1946, **65**, 95
[138] Fisher, C. H., Ratchford, W. P., Smith, L. T. and Fein, M. L., *Ind. Eng. Chem.*, 1942, **34**, 473; Fisher, C. H., Rehberg, C. H. and Smith, L. T., *J. Amer. chem. Soc.*, 1943, **65**, 763
[139] *Int. Sug. J.*, 1949, **51**, 320

[140] Ibid., 10, 96
[141] Lagomasino, J. M., ibid., 338
[142] Reich, G. T., *The Sugar Industry* (*Cuba*), 1948, **2**, No. 2, 6, 49
[143] Perdomo, E. V., Proc. 20th Meeting Assoc. Tecn. Azuc. Cuba, 1948, 467
[144] De Mattos, A. R., U.S.P. 2,541,156
[145] Barreto, A., U.S.P. 2,473,630
[146] Boinot, F., *Industr. agric. aliment*, 1948, **65**, 279
[147] Arroyo, R., *Sugar*, 1949, **44**, No. 7, 34
[148] Idem, *Int. Sug. J.*, 1949, **51**, 166, 189
[149] Guillaume, J., *Industr. agric. aliment*, 1948, **65**, 309
[150] Owen, W. L., *Int. Sug. J.*, 1949, **51**, 84, 109
[151] Herman, A., Izaak, J. A. and Bercuson, N., *Canad. Chem.*, 1949, **33**, 211
[152] Thaysen, A. C., Proc. Brit. West India Sugar Technol. Meeting, 1948, 21
[153] Sattler, L. and Zerban, F. W., *Ind. Eng. Chem.*, 1949, **41**, 1401
[154] Erb, C. and Zerban, F. W., *The Sugar J.*, 1949, **11** (12), 5
[155] Zerban, F. W., *J. Ass. off. Agric. Chem. Wash.*, 1949, **32**, 184
[156] Clark, G. C., Kao, H., Sattler, L. and Zerban, F. W., *Ind. Eng. Chem.*, 1949, **41**, 530
[157] Owen, W. L. and Owen, W. L., jun., U.S.P. 2,392,258
[158] Haworth, Sir N. and Stacey, M., B.P. 618,999
[159] Wiggins, L. F., 'Advances in Carbohydrate Chemistry,' 1949, Vol. 4, 293
[160] Idem., *Int. Sug. J.*, 1948, **50**, 65, 95
[161] *Chem. & Ind.*, **1949**, 555; *Int. Sug. J.*, 1949, **51**, 329
[162] Long, J., Technological Report No. 5, Sugar Research Foundation (N.Y., 1949)
[163] De Whalley, H. C. S., *Int. Sug. J.*, 1949, **51**, 223
[164] Eynon, L. and Lane, H., ibid., 168
[165] Gillett, T. R., *Analyt. Chem.*, 1949, **21**, 1081, 1084
[166] Estigneev, B. B., *Sakharnaya Prom.*, 1949, **23**, No. 6, 30
[167] Englis, D. T. and Miles, J. W., *Analyt. Chem.*, 1949, **21**, 583
[168] Stern, H. and Kirk, P. L., *J. biol. Chem.*, 1949, **177**, 37
[169] Podlubnaya, E. T. and Bukharov, P. S., *Zhurn. Analit. Khimii*, 1948, **3**, 131
[170] Eynon, L. and Lane, H., *Int. Sug. J.*, 1949, **51**, 169
[171] Whitehead, T. H. and Bradbury, W. C., *Analyt. Chem.*, 1949, **21**, 1430
[172] Dische, Z., Shettler, L. B. and Osnos, M., *Arch. Biochem.*, 1949, **22**, 169
[173] Ramanaiah, S. V. and Narasingarao, C., *J. Soc. Indian Res.*, 1949, **8B**, 99
[174] Hinden, S. G., Osterman, C. L. and Liggett, R. W., American Chemical Society (Philadelphia Section) Meeting for 1949, Advance abstr. 25
[175] Vavruch, I., *Listy Cukr.*, 1948–9, **65**, 171
[176] Zerban, F. W., Hughes, W. J. and Nygren, C. A., *Rev. Azucar Puerto Rico*, 1948, **2**, 47
[177] Heidt, L. J., Southorn, F. W., Benedict, J. D. and Smith, M. E., *J. Amer. chem. Soc.*, 1949, **71**, 2190
[178] Binkley, W. W. and Wolfrom, M. L., Scientific Report Series No. 10, Sugar Research Foundation (N.Y., 1948)
[179] Jermyn, M. A. and Isherwood, F. A., *Biochem. J.*, 1949, **44**, 402
[180] Hirst, E. L. and Jones, J. K. N., *J. chem. Soc.*, **1949**, 1659
[181] Hough, L., Jones, J. K. N. and Wadman, W. H., *J. chem. Soc.*, 1949, 2511
[182] Partridge, S. M., *Nature*, 1949, **164**, 443
[183] Horrucks, R. H., *ibid.*, 444
[184] Bliss, L. R., *Mem. Assoc. Tecnicos. azucar. Cuba*, 1948, **22**, 285
[185] Genotelle, J., *J. Fabr. Sucre.*, 1949, **90**, No. 10, 20
[186] Davies, J. G. *et al.*, 'A Manual of Sugar Analysis for Control Laboratories' (Jamaican Association of Sugar Technologists, 1948.)
[187] Bernhardt, W. O., *Proc. Amer. Assoc. Sugar Beet. Tech.*, **1948**, 547
[188] Othmer, D. F. and Luley, A. H., *Sugar*, 1949, **44**, No. 7, 26; *Food*, 1949, **18**, 81

THE FERMENTATION INDUSTRIES

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REFERENCE may be made to three important gatherings held in 1949. First, the Lucerne Congress of the European Brewery Convention, attended by some 200 delegates from 15 countries; the matters discussed fell under three main headings, viz. proteins in brewing, production of sterile beer by means other than pasteurization, and reports on barley investigations. A symposium entitled 'Recent Advances in the Fermentation Industries' was organized at St. Andrews by the Scottish Sections of the Royal Institute of Chemistry; edible and potable fermentation products were discussed, and sessions were devoted to such diverse industrial fermentations as distilling, butyl alcohol–acetone fermentation, 2 : 3-butylene glycol production, and the use of mould enzymes for saccharification. Microbiological advances were also included, covering microbiological assay methods and problems of aseptic technique in large-scale working.

The largest of these meetings was the First International Congress of Biochemistry organized at Cambridge by the Biochemical Society, one section of which was devoted to Industrial Fermentations including brewing and yeast manufacture, baking, silage, solvents manufacture and the like; individual meetings of other Sections frequently provided material of interest to the fermentation technologist or biochemist. Many of the papers read at one or other of these functions have appeared in the technical literature and will be referred to below. General accounts are also available in a number of Journals[1,2,3].

Reference to research schemes of a co-operative nature are being encountered with increasing frequency, and this is particularly true of late with regard to brewing research. Thus the formation of a Research Foundation is announced by the Master Brewers' Association of America,[4] while the Belgian organization V.E.B.O.[5] has been celebrating its 10th anniversary; this Belgian organization works in close co-operation with corresponding bodies in France (Secobrah) and the Netherlands. The Mid-West Barley Improvement Association of U.S.A. is doing useful work in stimulating the production of malting barley of enhanced quality (see below).[13] It may also be noted that some 200 N.C.T.C. yeast cultures formerly held by the Lister Institute have been taken over by the Brewing Industry Research Foundation; a list of the organisms, and the nature of the arrangements for obtaining cultures, have been published.[6]

Barley and malting

Agricultural problems relating to barley continue to be dominated by the introduction into Britain of the Danish varieties such as Kenia, Maja, etc., and by the related factors associated with the increasing use of the

combine harvester. A survey of the 1949 barley crop in Britain is available,[7] and a valuable general publication on the selection of malting barley has been made by Slight.[8] Useful contributions to the general discussion of the suitability of various varieties for British growing conditions are also provided by Hunter,[9,10] and two small monographs which have appeared during the year should be in the hands of all interested in the subject of barley for malting.[11,12] In brief, the consensus of opinion seems to be that despite certain superficial advantages, Kenia and related varieties are not altogether suitable for the barley-growing conditions in Britain; under very favourable conditions they may give excellent samples in high yield, but given less favourable circumstances results may be extremely disappointing. The established Spratt Archer and Plumage Archer, suitably chosen in relation to growing district, have probably not yet been bettered in this country, though the winter-hardy Pioneer shows some promise; new selections from the established varieties may prove useful, but it is not clear whether Earl—an early-ripening selection from Spratt Archer—will find general acceptance.

The value of winter-hardy and early-ripening varieties for producing a spread-over of the harvest period is clear, but emphasis continues to be laid[8,13] on the dangers of cutting too soon when the combine is used, and a number of associations set up to encourage the provision of malting barley of improved quality have also stressed the importance of proper threshing.[13,14] It is encouraging that some systematic attention has been given to problems associated with lodging; a study of this in cereals grown in Yorkshire and Lincolnshire suggests that it should be avoidable in nearly 90% of cases.[15] However, as this would involve growing stiffer-strawed varieties it should be remembered that, so far as malting barley is concerned, the choice should not be made at the expense of the malting characters of the grain. It is worthy of note that Kenia appears more susceptible to smut than the normal British varieties.[10] The modern practices of seed disinfection and fertilizer placement are resulting in an increased stand of cereal crops, and their effects need to be taken into account in deciding on the density of seeding.[12]

Investigations continue on the distribution of vitamins *B* in cereals; thus, nicotinic acid and riboflavin have been determined microbiologically in wheat[16]; whole barley (65–60 μg. per g.) contains some 2½ times as much nicotinic acid as does the chaff[17]; in the Canadian barley variety OAC 21, riboflavin increases initially in the grain but then decreases during ripening.[18] During storing, the vitamins *B* of grain remain stable for long periods, with the exception of thiamin which decreases by about 12% in five months.[19] In an important study of wheat, barley and oats along new lines, McElroy *et al.*[20] find variability in the amounts of nitrogen representing individual amino-acids, even in different samples of a variety; this result might have been forecast from a consideration of Bishop's 'principle of regularity,'[21] and may need to be taken into account in assessing the yeast-feeding properties of worts (see below).

The heavy volumes of grain which are coming forward in a restricted period as a result of combine harvesting are creating serious storage problems, especially in seasons when the moisture content of threshed barley is high. Attention has been given to avoiding the use of farm

driers, as by using aerated bins carrying a current of air at a temperature a few degrees above that of the atmosphere[22,23,24]; for avoidance of mould growth it is important that the saturation of the air passed through should not exceed 75%.[24] A detailed account of the principles and practice of silo construction, both on conventional lines and with aeration, is given by Jolley.[24] Short period storage at 75% humidity is considered safe.[25] A device is described by Carr and Hadley[26] in which the rate at which grain is passed through a drier is controlled electrically by the moisture content of the grain.

Insect infestation of stored grain may be a tremendous source of loss, and important data on insecticidal action are being accumulated. Mixtures of chlorinated hydrocarbons are effective against *Calandra granaria* and similar insects; best results for the treatment of empty sacks have been obtained with a mixture of 3 parts of $C_2H_4Cl_2$ and one part (vol.) of CCl_4.[27] Again, it is claimed[28] to render grain immune from insect infestation by treating it with air which has been passed at 40–50° c. over hexachloro*cyclo*hexane. The cereal and grain moths *Sitotroga cerealella* and *Corcyra cephalonica* can be controlled under enclosed conditions by the sweet flag (*Acorus calamus*).[29] A valuable account of the Khapra beetle and of methods for its elimination or control in maltings is provided by Price[30]; use is described of 5% DDT and 1% hexachloro*cyclo*hexane in odourless kerosene and of a 1% aqueous emulsion of DDT. Clearing for useful periods is possible.

Growth and germination inhibitors have been studied from a number of viewpoints. Thus, no relationship appears to exist between dormancy in seeds and the power of extracts to inhibit germination; bean-meal contains a non-dialysable, chloroform-insoluble growth inhibitor which is stable to heat, and extracts of a wide range of non-dormant seeds inhibit the growth of wheat rootlets.[31] 1-naphthylacetic acid and some aryloxyacetates in small concentration kill charlock or retard its growth, but have no effect on cereals.[32] A small influence of compounds of this type when used in the steep in concentrations of 25–200 p.p.m. can be shown during the malting of barley.[33]

A preliminary study of barley phytin is provided by Sandegren.[34] A particular Swedish variety grown at a single station showed little annual variation in phytin content, but there were large differences when the same variety was grown at different stations. Phytin in barley is originally water-soluble, but it becomes at least partly insoluble on steeping, and during the course of malting some 20–30% is hydrolysed. Attention has been given to the design of malting equipment, and there is increasing interest in the provision of mechanical devices. The mechanization of maltings is critically discussed by Cherry-Downes,[35] who deals with such problems as barley intake, drying and storage (see above [22–26]), and with the malting process itself from steeping to malt storage; the account concerns itself with the Saladin and drum systems as well as with the traditional flooring. Modified kilns provided with grain turners and with mechanical devices for discharge of barley or malt have been described[36]; control of temperature and drying rate, of thermal diffusion, and of flexibility of operation has been improved in a multi-stage kiln[37] by making the circulating air system independent of each

stage; the kiln can be used for drying grass, sugar beet pulp, etc., as well as for malt.

Hops

In a short account of hop-growing in the West Midlands, Wilkinson[38] gives a useful introduction to the study of hop cultivation problems. Though the fluctuating form of *Verticillium* wilt is present in this area, the progressive form—which has caused so much concern elsewhere—is apparently absent. In his 1947 report on new varieties, Salmon[39] notes that several have a measure of resistance to *Verticillium* (*see* also Keyworth[40]), and two of them—OR 55 and OJ 47—are to be grown on a large scale, since they have given satisfactory results in preliminary brewing trials.[41] The variety OT 48 is also strongly recommended for future trials[42]; it has some resistance to *Verticillium* and has given satisfaction in small-scale brewing trials. Some characters of the fluctuating wilt have been described.[43,44] Late dressing and training gave a reduced attack by the fungus, and a year-by-year study in a single field suggested localized attack in particular areas, probably due to differences in soil conditions.

Attack by nettlehead also seems to be confined to localized areas and may be associated with particular soil types, though the nutritional status of the plant with respect of NO_3, P, K, Ca, and Mg is apparently unrelated to the incidence of this disease.[45] An aerial survey of hop gardens attacked by nettlehead showed that the symptoms were often most prominent on the sites of old hedgerows; in other cases, the disease was greater on land that had formerly been pasture than on old arable land.[46] Mosaic disease has been studied from the point of view of tolerant and sensitive varieties,[47] whilst means have been developed for testing the reaction to the disease of male hops and new seedlings. A comprehensive résumé of hop diseases in the U.S.A. is provided by Hoerner.[48]

It is said in Belgium that hops suffer from water deficiency one year in three, and Lambert[49] considers that artificial irrigation would benefit both quality and quantity of crop, pointing out also the importance of proper working of the soil and placement of fertilizers chosen with regard to solubilities. From a study of the distribution of bitter acids it is found[50] that α-acid is formed mainly during late August and early September, apparently at the expense of lupulon. If oast treatment does not allow the temperature to exceed 50° c., drying can be accomplished without loss of humulon or lupulon, but handling immediately after drying can cause considerable loss. From a study of storage deterioration of Zatec hops over a period of 12 months, Goedkoop[51] concludes that, to obtain the same bittering effect, storage at 0° c. necessitates the use of 18% more hops, and storage at 6–8° c. 39% more. It may be suggested that generalization should not be made from a single series of experiments, since there is every reason to suppose that storage persistence of α- and β-acids and soft resins depends not only on the variety but also on seasonal considerations which remain at present quite obscure.

Siegfried[52] advocates the maximum elimination of tannin from wort, and this is best achieved by using hops with low resin content and by suitable choice of hopping methods. Kolbach[53] notes the removal of

substantial proportions of bitter principles with the coagulum from wort and beer and with the yeast. Recovery of useful principles can be effected by mixing coagula with fresh hops or by extracting the wastes with water (preferably not decarbonated) or with organic solvents.

Govaert[54] finds that the resins which are formed from the bitter acids contribute no bitterness to beer; humulon has greater bittering power than lupulon, though humulon itself is ineffective. During boiling, humulon is in part converted to *iso*humulon of enhanced solubility and bittering power. Neither humulon nor lupulon can be detected in beer, but *iso*humulon has been found; it is possible that isomers may also be formed from lupulon, but their influence is extremely small. It is thus confirmed that the effective principle in the original hop is humulon, indirectly supporting the present British convention of assessing the value of a hop on the basis of α-acid alone. A hopping method based on the isomerization is described by de Clerck[55] who also quotes formulae for humulon and its active isomer. Hops are pretreated in an alkaline medium before addition to the copper; the procedure was originally claimed to effect a 50% saving in hops, but de Clerck, although confirming that economy is effected, finds a smaller saving than this.

The hops of the 1948 season are reviewed by Richardson[56]; the quality of the crop was not high, as might be expected with a wet growing season and frequent low temperature. Spraying treatments for the control of mildew and insect pests seem to be increasingly effective, but the ravages of *Verticillium* continue to cause concern. Prospects for the 1949 season, as adumbrated by Myer,[57] seemed better so far as quality was concerned, though the dryness of the season would undoubtedly reduce the yield; a survey of the 1949 crop is given by May.[58]

Biochemistry

Starch and amylases.—Further studies on the fractionation of potato starch by ball mill grinding and aqueous extraction have been made by Lampitt *et al.*,[59,60] notable differences in behaviour being found between this starch and that of wheat. Grinding causes depolymerization and the molecular weights of the fractions can be obtained from the viscosities of extracts; depolymerization affects the unbranched portions of amylose and amylopectin molecules. Potato amylopectin is richer in phosphate than potato amylose, and contains almost all the starch phosphate in a strongly bound, esterified form; in wheat starch the phosphate is less strongly bound, being chiefly adsorbed on the amylose as phospholipin.[61]

The importance of electrolytes, especially phosphates, in starch degradation is insisted on by le Corvaisier,[62,63] who considers that the duality of malt α- and β-amylases is not established; he visualizes the existence of esterified and non-esterified chains in starch structure, saccharification involving the hydrolysis of the latter by amylase. Liquefaction he regards as probably the joint action of amylase and phosphatase.

A more generally acceptable view of starch structure and amylolysis is presented by Myrbäck[64] who stresses the importance of 'anomalies' (branch points) in amylopectin, these representing principally points of attachment of side chains of glucose units, though some of the anomalies

may represent linkages with phosphoric acid. Neither α- nor β-amylase can hydrolyse these branch points,[64,65] which therefore are still present in the limit dextrins which accompany glucose and maltose when starch is submitted to amylolysis; it is therefore to be expected that, as conversion proceeds, the complexity of the limit dextrins will progressively decrease till they are ultimately represented by a mixture of a disaccharide (*iso*maltose) and a trisaccharide (maltotriose).

A detailed study of amylolysis by mixture of α- and β-amylases, and by α-amylase alone, has been made by Preece and Shadaksharaswamy,[66,67] under conditions simulating in some respects those of brewery mashes; it is emphasized that results identical with those obtained under brewery conditions are not to be expected, owing *inter alia* to the unknown influences of concomitants and starch type, though comparative results of high utility appear to be obtained. The influence of heat instability of β-amylase is well shown, though this enzyme is more stable in malt extract than in aqueous solution containing the minimum of concomitants. The D.P. value is probably a better guide to the amylolytic potentialities of a malt than a comparative knowledge of α- and β-activities. The dextrinizing and saccharifying actions of α-amylase are probably independent functions, though they overlap in practice; dextrinization produces dextrins with a mean molecular size of 8 glucose units, corresponding to a reducing power of $\sim 25\%$ (as maltose), the values of 30–33% usually quoted being due to concurrent saccharification which has occurred up to the inflection point. In a study of the hydrolysis of waxy maize starch by pancreatic (α-) amylase, Mindell *et al.*[68] have investigated the complexity of the products at various stages of hydrolysis and have shown the influence of enzyme concentration on the apparent inflection.

The long-standing controversy as to the presence of *iso*maltose and of one or more trisaccharides in starch hydrolysis products, and therefore in mash tun wort, seems to be nearing its solution. Thus, Montgomery *et al.*[69] have isolated 6-(α-D-glucopyranosyl)-D-glucose (*iso*maltose) from the products of exhaustive hydrolysis of waxy maize starch with taka-diastase; the sugar was unfermentable by yeast and gave $[\alpha]_D^{24°} + 103{\cdot}2°$ in aqueous solution. The presence of 1·6 linkages in the branching component of starch is thus confirmed. Wolfrom *et al.*[70] hydrolysed waxy maize starch with malt amylase, and isolated the crystalline hendeca-acetate of a trisaccharide, the structure of which is given by Sugihara and Wolfrom[71] as 4-[-4-(α-D-glucopyranosyl)-α-D-glucopyranosyl]-D-glucopyranose; this sugar, in water gives $[\alpha]_D^{23°} + 160°$; it is not hydrolysed by emulsin, and maltase gives a mixture of glucose and maltose. Indirect evidence for the existence of such a 'normal' (straight-chain) trisaccharide in wort is also provided by Blom and Schwarz,[72] their sugar giving a similar value (indirectly determined) for $[\alpha]_D$; they also confirm the presence of glucose in starch conversion products.

Since the 1:6-linkage is attacked neither by α- nor by β-amylase, complete conversion of starch to glucose and maltose by a mixture of these cannot be expected. This may be the reason why mould bran gives slightly greater yields of alcohol when used for distillery amylolysis, since *iso*maltose appears to be unfermentable,[69] and the well characterized

'normal' trisaccharide only slowly fermentable by yeast; the slow fermentation may be responsible for secondary fermentation under lager brewery conditions.[72] It must not be forgotten that one (or perhaps two) 'anomalous' (branched) and therefore unfermentable trisaccharides may also be formed. Tsuchiya *et al.*[73] have shown that *iso*maltose is hydrolysed to glucose by the action of a culture filtrate of *Aspergillus niger* N.R.R.L. 330. Similarly, Kneen and Spoerl[74] and Witt and Ohle[75] give evidence for the existence of a limit dextrinase (1 : 6-glucosidase?) in distiller's (low dried) malts but not in brewer's (high dried) malts; such an enzyme would enhance alcohol production under distillery conditions but would have no brewery significance.

Other carbohydrates.—Methods for the production of dextran have been described, using *Leuconostoc mesenteroides*[76] or *Betacoccus arabinosaceus*,[77] with a nutrient medium containing sucrose in each case. Study of the crystallizable Schardinger (*macerans*) dextrins has been carried out by French *et al.*[78]

Proteins.—The seed globulins of 9 species of Gramineae have been examined by Danielsson,[79] Quensel's method of salt extraction being used, followed by fractional precipitation with ammonium sulphate, dialysis, and study at the ultracentrifuge. Well-defined α- (mol. wt. 29,000) and γ- (mol. wt. 210,000) fractions were obtained, the former from six species including wheat and barley and the latter from wheat, barley, and six others; β- and δ-globulins were found in barley only. The distribution of the fractions suggests that γ predominates in seeds with little reserve protein; attempts to prove α a product of degradation of γ have failed. The β-globulin is associated with chill-haze formation in beer. In view of the modern importance of physico-chemical techniques, the comprehensive survey of them by Maestenbroek[80] as applied to proteins will be welcome. Also, Thuman *et al.*[81] have studied protein foams obtained by bubbling air through suspensions under a variety of conditions. Ions of alkaline earth metals enhance foaming in the alkaline range, but may diminish it on the acid side. Maximum foaming would seem to need a minimum unit charge on the protein particle by suppression of ionization at high or low p_H values, by self-neutralization at the *iso*-electric point, or by the neutralizing effects of anions or kations. Foaming behaviour in its general characters does not seem to differ from other protein properties.

Barley proteins and nitrogen compounds in general in their relation to the brewing process are discussed by Bishop.[82] A useful contribution is also provided by this worker's fractionation of the nitrogen compounds of wort and beer by precipitation with increasing amounts of phosphotungstic acid.[83] The precipitation is discontinuous and a range of products of contrasting properties is obtained, these being characterized by their content of free amino nitrogen; it appears that compounds are present in wort yielding 1, 2, 4, 8, 15–16, and approximately 30% of free amino nitrogen; in beer, the simpler of these compounds are absent or diminished in amount as a result of utilization by yeast. Hopkins and Berridge[84] find the outstanding character of the coagulable protein of sweet wort to be its susceptibility to calcium salts, which enormously increase its rate of coagulation. The coagulation seems to

catalyse itself and is also favoured by low p_H values, the coagulum carrying down with it variable amounts of nucleic acid. In the light of their results, these authors review the earlier findings of St. Johnston,[85] and in particular the reported interconversion of his protein fractions C (coagulable) and O (oxidized); the colour of the latter may be due to impurities, but the alleged reduction of O to C by calcium bisulphite may be due to the influence of calcium ions on coagulation rather than to a bisulphite reduction. It seems that a consideration of such results against the background of the work discussed earlier[79,83] might be worth while. The calcium relationships of proteins are worthy of further study; Bonot[86] notes that excelsin fixes calcium to an extent dependent on the ionization of the protein and the concentration of calcium salt in the liquor.

Enzymes and fermentation.—The isolation and purification of barley and malt amylases has been studied by Danielsson and Sandegren,[87] these enzymes being associated with the albumin fraction of the grain proteins. Despite their different activities, the sedimentation constants of enzymes from the two sources are the same, but at 1° C. the α-amyase separates more readily than the β; electrophoretic attempts at separation were unsuccessful. The position is further reviewed by Lundin.[88] The preparation of crystalline α-amylase from malt is described by Schwimmer and Balls,[89] the method involving adsorbing the enzyme from a 40% alcoholic solution on starch, thereafter eluting and crystallizing by adding ammonium sulphate to a solution at 30° C.

The value of pectic enzymes in wine treatment is discussed by Cruess and Kilbuck,[90] enhancement of both quantity and quality being achieved with their help. Beaven and Brown[91] show the presence of a disaggregating pectic enzyme complex in the mould *Byssochlamys fulva*, unaccompanied by glycosidase; distinction between disaggregation and saccharification may prove of general validity in the polysaccharide enzyme field. Continuing earlier studies, Wallerstein *et al.* report the presence of an *o*-phenylenediamine oxidase in rice, wheat, and maize[92] and various malt adjuncts (rice, maize, barley, wheat) contain a peroxidase,[93] the amount of which increases during malting, especially in the rootlets and acrospire; both enzymes may show a degree of survival after kilning (when malted) and mashing, and so may contribute to mash changes. The purification and storage of *Q*-enzyme of potato has been reported on[94] and the characters of the enzyme have been studied[95]; Bourne *et al.*[96] have investigated further the synthetic activity of potato phosphorylase (free from *Q*-enzyme), and have shown the importance of chain length in the polysaccharides acting as activators for this enzyme. In the opposite direction, phosphorylase cannot attack 1·6 linkages (*cf.* above), and the course of degradation shows some resemblance to that brought about by β-amylase, differing markedly from that with α-amylase.

Pointing out the possible alternatives of phosphorolysis (though the appropriate enzyme has not been found in yeast) and polymeric cleavage, Hestrin[97] suggests that the intervention of maltase may be unnecessary in maltose fermentation; several paths are theoretically possible. Similarly, lactose fermentation can proceed under conditions which appear to preclude lactase action, and trehalose fermentation may possibly

not involve preliminary hydrolysis to glucose; the position of melibiose is obscure. The theory of direct fermentation of disaccharides is contested by Gottschalk,[98] who considers that the evidence adduced in its favour is capable of other interpretation and that difference in permeability of the yeast cell to different sugars and glycosides is an important factor. Possible modes of cleavage of sucrose are also considered by Hestrin,[99] the review relating in its direct evidence to bacteria (*Leuconostoc mesenteroides* and *Pseudomonas saccharophila*) rather than to yeast, since in the latter case the preponderating action of invertase would obscure other modes of breakdown.

The relative rates of fermentation of glucose and fructose have been studied by allowing yeast to come into only momentary contact with dilute sugar solution; at 15° C. glucose disappears the more rapidly, and fructose solutions substantially free from glucose can be obtained. When sucrose is used, fructose disappears the more rapidly owing to the rapid attack on the liberated furanose form.[100] These results are in accord with earlier findings of Gottschalk.[101] The acetylmethylcarbinol formed in *Acetobacter aceti* fermentations arises from quantitative oxidation of butane-2 : 3-diol and also, in small amounts, from lactic and succinic acids.[102] Sulphur dioxide production in alcoholic fermentation, the result of inadequate provision of nutrient salts, can be avoided by adding $(NH_4)_2HPO_4$.[103] A yeast adapted to ferment galactose gave an extract which, in presence of adenosine triphosphate, fermented glucose and galactose at approximately equal rates. Galactokinase is present in such adapted yeasts and produces galactose-1-phosphate; glucose-6-phosphate is probably formed intermediately between this ester and fructose-1 : 6-diphosphate (Wilkinson[104]). Pointing out the importance of triose phosphates in the fermentation of sugars, Kiessling[105] states that their production is accelerated by an extract of *Aspergillus niger* mycelium and the rate of fermentation is simultaneously increased.

Vitamins in cereals and fermented products.—Reference has already been made to certain vitamin studies on cereals,[16–20] but attention may be further directed to the finding of Spencer *et al.*[106] that despite standardization of assay methods, small consistent and significant differences occur between different laboratories; differences of 10–12% in mean assay figures are necessary before thiamin or riboflavin results can be considered significantly different in analyses of barley, wheat and oats.

Riboflavin can be recovered from whey after fermentation with *Clostridium acetobutylicum* in presence of added salts and *p*-aminobenzoic acid; pretreated sulphite liquors or wood hydrolysates can be used as sources of sugar.[107,108,109] Penicillin-extraction mother liquor, concentrated to a syrup, combined with the mycelium, and dried to form a supplementary animal and poultry food, gives a product rich in vitamin *B* complex.[110] Slop from whisky distilleries is enriched with vitamins *B* by fermentation with selected genera of *Aerobacter*.[111] In riboflavin production by *Candida* yeasts (Levine *et al.*[112]) given low iron content in the medium, ammonium sulphate and/or urea can be used as sole nitrogen source; various salts (other than iron) produce no inhibition. Pure chemicals need not be used, nor is sterilization of the medium necessary. Atkin[113] notes variations in the bios requirements of different

yeasts; the vitamins concerned are inositol, pantothenic acid, biotin, aneurin, pyridoxin and nicotinic acid. Tetraploid yeasts retain more nicotinic acid and excrete less than do diploids, though total production of the vitamin is approximately the same in the two cases.[114]

Yeast

The factors influencing sporulation in yeast (Phaff and Mrak[115]) include the conditions of culture used, oxygen availability, temperature, p_H, moisture, genetic factors, and the composition of the medium with respect to carbohydrates, nitrogen compounds, metabolic products, and trace elements; appropriate sporulation media are described. Study of the formation and characters of the spores is fundamental to classification, and of particular interest is the point at which diploidization takes place. Genetic considerations relating to spore formation and diploidization are discussed by Winge and Roberts[116] in connexion with the 'yeast foam' strain of *S. cerevisiae*, in which single spore cultures rarely diploidize, and *S. chevalieri* where diploidization in single-spore cultures is the rule. The fermentation of trehalose is proposed as a character of taxonomic significance by Bouthilet *et al.*[117]; it is of particular value with *Candida* yeasts, though other genera also contain strains fermenting this disaccharide. Trehalose has been isolated from yeast by Stewart *et al.*, [118] and the presence of this sugar in baker's yeast extracts may lead to unreliable results when they are used as basal media in testing sugar fermentations[117]; the use of autolysed yeast would be better, though extracts of brewer's yeast (from which trehalose is absent) often proves satisfactory.

In a simple inexpensive method for preserving yeast, Mueller[119] uses 2–3-l. Erlenmeyer flasks containing sterile 10% sucrose solution into which massive portions of washed, pressed yeast are introduced under aseptic conditions; with storage at 4–5° c., viability is retained indefinitely. Laufer and Mohr[120] isolate yeasts as single-cell strains, propagate them in tubes and Pasteur flasks, and finally transfer to modified 7–8-l. Carlsberg vessels made of glass. For shipment, the liquid yeast is aseptically transferred to 2-l. stainless steel vessels provided with two outlets controlled by needle valves.

It has been found possible to classify yeasts according to their bios requirements.[121] Yeasts of the five groups require: (*a*) biotin only (*b*) biotin and pantothenate (*c*) biotin and inositol (*d*) biotin, pantothenate and inositol (*e*) biotin, pantothenate, inositol, and aneurin or pyridoxin. Lager yeasts belong to the first four groups, but ale yeasts are of type (*e*). Although the bios factors so markedly affect growth, they have little effect on fermentation under the conditions used, but to maintain attenuation at the proper rate it seems that a definite rate of yeast growth is necessary, when inositol is of dominant importance. Inositol deficiency is unlikely to be met in practice, since wort contains some 20 times the limiting concentration, but it is not improbable that anti-inositol factors may exist. Examining the factors affecting the growth of pure culture yeast and its nitrogenous composition, Clark[122] finds that the nitrogen content is increased by increasing the amounts of carbohydrate and assimilable amino-nitrogen available; the effects of salts are variable,

but alcohol production increases with decrease in total nitrogen, this decrease taking place in nitrogen groups other than mono-amino. Again, van Lanen *et al.*[123] showed that proteolytic enzyme preparations (papain, ficin, culture filtrate from *B. subtilis*) could replace part of the malt used for mash conversion in distilling practice without loss of alcohol yield. The effect is associated with yeast nutrition rather than with enhanced amylolytic extraction or activity; possibly the provision of greater amounts of assimilable amino-acids of special types is the effective factor, and a similar useful result might be obtained by using malts of greater proteolytic activity.

Thorne has shown[124] that top fermentation yeasts differ in bios requirements, and that small differences also exist in a particular yeast according to the source of nitrogen. Damlé and Thorne[125] find that certain dipeptides are some 10% less efficient as nitrogen nutrients for yeast than mixtures of the corresponding amino-acids, and hydrolysis would appear necessary before use. Taylor[126] finds arginine, glutamic acid, histidine, lysine, ornithine and tyrosine present in the free state inside yeast cells, even though the cells are grown in absence of amino-acids. Glutamic acid uptake requires energy provided by glucose fermentation, and is decreased in presence of ammonium salts and some amino-acids.

It has long been assumed that yeast uses amino-acids by deamination (Ehrlich mechanism), the ammonia being employed for resynthesis. Thorne[127] now shows that neither this mechanism, nor the similar Stickland mechanism (involving simultaneous oxidation–reduction of certain pairs of amino-acids), nor the two together, suffice to explain the observed facts of amino-acid assimilation from complex mixtures such as are provided by wort or other 'natural' nutrients. He proposes a third mechanism, that of direct assimilation. Thus, from an adequate mixture, amino-acids would be assimilated as required; from a mixture deficient in some amino-acids, direct assimilation would take place as far as possible, but a proportion of the amino-acids would be deaminated by the Ehrlich or Stickland mechanism to provide ammonia for the synthesis of those missing. Much evidence supports this; it is known that mixtures give better results than single amino-acids, and it is shown that with mixtures more alcohol is produced in fermentation since less sugar is required for synthetic processes. Further, pyridoxin deficiency is of less marked effect with mixtures than with single acids, and this is related to the supposed function of this vitamin in deamination.

In further support, Barton-Wright and Thorne[128] show that, with wort as the growth medium, amino-acid assimilation represents some 70% of the total nitrogen uptake, and for a number of amino-acids assayed microbiologically in the wort at intervals during fermentation, the uptake is in proportions closely correlated with the amino-acid distribution in the yeast cell itself; also, yeast cannot deaminate lysine and histidine, and yet assimilates them very readily. The evidence thus appears conclusive; deamination, oxidation–reduction, and direct assimilation occur side by side to relative extents which depend on the types of nitrogenous compounds supplied.

Numerous references relate to the production of food yeast. Schmidt[129] reviews the production of protein yeasts and fat yeasts from sulphite

liquor, and Floro *et al.*[130] describe anew the operation of the Thaysen process in Jamaica. The possibility of using sugar cane bagasse is discussed by Vasquez,[131] and it is calculated that 3·5 tons of dry bagasse should yield 1 ton of cellulose and 0·5 ton of yeast. The process involves digestion of the bagasse with 0·3% sulphuric acid at 135° c. for 1 hour, neutralization with press cake, and fermentation with *Torula utilis*. The use of wood hydrolysates is of great interest, and Harris *et al.*[132] digest wood with 0·5% sulphuric acid at 150–185° c., neutralize with lime and remove volatiles by distillation; with continuous agitation and efficient use of oxygen in deep vessels, satisfactory results are obtained in a throughput time of 3 hours. *T. utilis* grows almost equally well on a variety of hydrolysates, but baker's yeast will not develop on oak hydrolysate. Acclimatization of various yeasts to wood sugar can be accomplished by repeated transfer at 24-hour intervals to fresh medium[133]; sugar utilization from Douglas fir is eventually 78–94%, with yields of alcohol of 31–40% and of yeast 30–42%. The influence of growth conditions on food yeast production is described in detail by Singh *et al.*[134] and, with yields of yeast varying from 4–75% of the sugar utilization, the protein content is unaltered; however, vitamins B_1 and B_2 decrease and niacin increases with increased yield. Further discussions of interest are provided by Bunker[135] and Zagrodzki[136]; a maize steep liquor concentrate suitable for the growth of yeast, moulds, and bacteria has been patented.[137] The food value of microbiological protein derived from waste yeast, butyl alcohol–acetone fermentation residues, and waste mycelium from penicillin manufacture is reviewed by Braude,[138] who sees no reason for neglecting any of these. Finally, van Laer[139] notes the importance in yeast manufacture of feeding young yeast with small quantities of sugar at a time to prevent the accumulation of fermentation products, the necessary rate of addition being governed by the activity of the enzymes concerned in the synthesis of yeast cell substance.

Bacteriology

Continuing his study of ropiness in beer, Shimwell[140] deals with lactobacilli, describing the characters of *L. pastorianus* var. *brownii*, isolated from a ropy bottled ale. When first observed, this organism caused ropiness in bottled beer saturated with carbon dioxide, but the character was lost after prolonged maintenance as a stab culture. It appears that, with this organism, the predisposing factors in beer leading to ropiness would be the presence of glucose and maltose and a high carbon dioxide concentration. Another ropiness organism is *Streptococcus mucilaginosus* Kulka, Cosbie and Walker (*spec. nov.*)[141] which is detrimental to beer under both aerobic and anaërobic conditions and has retained its viscous propensities after 5 years of laboratory cultivation. Kulka *et al.*[142] propose cultivation of *Acetobacter* spp., on semi-solid wort agar, when some species assume characteristic growth forms which aid in their identification. Dark-ground illumination of giant colonies on this medium is helpful, and so is photography by top-lighting. In an attempt to trace the cause of a woody flavour or mustiness in certain draught beers, Brown *et al.*[143] found that the casks concerned were infected with a species of *Actinomycetes*, resembling *Streptomyces griseus*. The organism does

not grow in beer, but develops in the wood of the cask when empty, the unpleasant flavour being communicated to beer on subsequent filling. Ordinary washing of casks does not eliminate the trouble, and infection may be spread from the washing yard and by the brushes of the cask-washing machine.

Helm,[144] examining 615 samples of wort from different breweries, found bacteria in 40% of them. 95 growths were of *Aerobacter* and *Escherichia* spp. 20 *E. coli* were indole-positive and 6 indole-negative; the latter gave a phenol-like taste in beer if infection by the organism sufficiently preceded addition of yeast. Other members of the *coli-aerogenes* group can cause celery-like or mushroom-like flavours in beer. The importance of personal cleanliness is stressed as are also the need to to start fermentation as soon as possible after boiling and to seek regularly organisms of the types mentioned. Comprehensive reviews of brewing bacteriology are provided by Shimwell[145] (Lactobacteriaceae and also common but harmless brewery bacteria) and by Walker and Kulka[146] (*Acetobacter* spp.). Sampling techniques for wort and beer are described by Olshausen[147] and in a review of brewery methods for bacteriological control Chevalier[148] doubts whether coliform bacteria are, in fact, detrimental to beer and advocates the use of pasteurized beer or, better, specially sterilized beer in tubes or flasks plugged with cotton wool, as routine test medium; addition to this of yeast water improves its value for detecting 'beer sarcina,' lactobacilli, and wild yeasts. Methods for detecting specific types of organisms are treated in some detail.

Beer and brewing

An admirable and detailed general account of modern brewery design, equipment and operation is given in Plumpton's description of the Park Royal Brewery.[149] In a process claimed to give beer with a smoother and pleasanter hop flavour, Seng[150] treats sparge water with a slurry of gypsum in the pipe-line leading to the sparge arm, top pressure of carbon dioxide being used for transferring the slurry. The importance of water-treatment and of careful control of all subsequent stages of the brewing process is stressed by Chabot[151] in discussing the maintenance and improvement of beer quality. Beer stability and character are intimately bound up with the treatment the wort has undergone; the role of wort boiling in this connexion has always attracted attention, and the interactions of proteins and tannins in particular merit consideration (*cf.*[82–85]). Luers[152] considers the problem anew, suggesting that hop tannin is undesirable in beer, and recalls a process in which ground hops are extracted with cold water and the extract treated with active carbon before use; the process not only improves colour and flavour but enhances cold stability. Scalding the hops with hot water before use removes some 40% of the tannin, and the beers are of finer flavour. The influence of fermentation changes on flavour is also discussed.[153]

Colloidal hazes, according to de Clerck,[154] are due to oxidation of complex proteins or to the action of tannin or of traces of heavy metals. Stability can therefore be assessed from the content of complex proteins determined by some appropriate precipitation method (*cf.*[83]) and the degree of oxidation found by the indicator–time test; heavy metals and

tannin can also be determined. Even with all this information, unknown factors preclude proper interpretation of the results; storage of beer at 40–60° c. is as good a test as any. If the beer proves unstable, the more detailed examination indicated may tell why it is so. Progressive changes in air content of wort and beer have been studied by Smith,[155] who concludes that the optimum content of air in beer is about 3 ml. per l.; to obtain this, closed fermenting vessels should be used, top pressure applied with carbon dioxide of 99·95% purity, and filled bottles made to foam by knocking. A comprehensive review of the applications of redox potential to beer problems is given by Rippel,[156] and Urion combines a discussion[157] of this with a survey of the importance of p_H. The increase in r_H during racking is due to oxygen carriers (iron and copper ions) in the beer, and the important subsequent slow fall is brought about by such substances as melanoidins and reductones, these exerting a buffering effect against undue redox changes when ultimate equilibrium is reached. The reducing substances are derived chiefly from malt, some may come from caramel, and others may be formed during wort boiling. The influence of r_H levels below 13 in favouring the development of sun flavour is combated by using amber bottles. The characters and origins of reductones are described in some detail by Hugmann[158]; the amounts of these and of melanoidins in wort are increased by prolonged boiling and their effect is most marked in dark beers. Special r_H patent malt is available, giving a wort highly stable towards oxidation. The importance is stressed by van Roey[159] of conserving natural reductones; the possibility of adding these to beer immediately before bottling is noted. A method for determining air in bottled beer is given by Urion and Lejeune,[160] and the papers by Hartong[161] and de Rijck[162] may also be consulted on the general redox problem.

The excessive escape of carbon dioxide from beer leading to troublesome fobbing is discussed by Beattie,[163] who indicates the complex relationships existing between proportions of carbon dioxide and air, agitation, the presence of colloidal materials including denatured proteins, dirt in bottles, and temperature changes. A relation between undesirable fobbing and desirable head will be obvious, but its exact nature is obscure. The essentials of foam formation in beer are dealt with in a practical way by Becker,[164] who shows the liability of excessive modification in malting to lead to poor foaming properties, though hop rate and the nature of the yeast also play a part. Traces of grease carried over from compressors may cause trouble. For assessing foaming properties, simple pouring of beer is preferred to the more complicated 'scientific' methods. A method for controlled carbonation of beer is described by Hagues,[165] providing plant which is readily cleaned and simply operated. A valuable discussion of beer storage and dispensing appears in a review by Scott,[166] who proposes methods designed to improve and accelerate the service of draught beer.

On the biological side of beer stability, the works dealt with under 'Bacteriology' may be recalled,[140–148] and attention drawn to a contribution by Moortgat[167] on the problem of sterile bottling following sterile filtration; comparing this method with pasteurization, the author prefers filtration on the grounds of flavour and colloidal stability, but pasteurization is

more certain in achieving biological stability. A practical method for pre-bottling pasteurization and sterile filling is described by Watkins.[168]

Yeast infections of beers have received too little study, so that papers by Wiles[169] are particularly welcome. Methods are described which were successful in tracing the cause of yeast deposit in some bottled beers. Infection developing overnight in the filling machines could be avoided by antiseptic treatment based on the use of very dilute chlorine solution. A number of yeasts, chiefly varieties of *S. cerevisiae*, but differing markedly in character from the normal pitching yeast, were encountered and described. Widespread beer haze encountered in many parts of Britain during the summer of 1948 was traced to a yeast which has been described as a strain of *S. carlsbergensis* (Yorkshire haze strain I). The haze appeared soon after the beers arrived at licensed premises (though they were brilliant on arrival).

Because of shortages of raw materials for brewing in some countries preparations from beet have been used as sources of fermentable sugar, though it is surprisingly stated that even 99·8% pure beet sugar gives undesirable flavour to beer.[170] A substitute drink from malt and hops described by Ernst[171] contains 0·3–0·4% of alcohol, and the difficulty in its production is to balance palatability against production efficiency. Klein[172] employs albedo (from citrus fruits) and hop resins (where desired) to produce beer without the use of whole hops. A variety of substitute beverages have been manufactured in Germany.[173] The adaptation of conventional brewing equipment to the production of other food materials is described by Zunterer.[174] An admirable survey of the overcoming of production difficulties is found in de Clerck's account of Belgian brewing during and after the war.[55] Points of outstanding interest include methods in use or contemplated for reducing malting loss and for economizing in hops. Top yeasts have been found able to adapt themselves in a surprising degree to worts of low gravity, and it is doubtful whether occasional propagation in strong wort serves any useful purpose. The paper is full of interesting information, and cannot adequately be summarized. The brewing of Kaffir beer from Kaffir corn, millet, and bulrush millet is described by Young[175]; the product contains 3–3·5% of alcohol and about 20% of suspended solids, and provides a valuable source of vitamins and salts.

Plant; detergents

Plumpton's report[149] on the Park Royal Brewery should be consulted for a general description of brewing plant. On specific matters, Smith[176] shows how, apart from obvious losses, inefficient heat insulation gives excessive amounts of wet steam and causes corrosion of plant; magnesia has advantages as insulating material when reinforced with asbestos. An unusual material which has been successfully used in a particular case for insulating the walls of fermenting cellars is balsa wood.[177] Heat-exchange problems in connexion with pasteurizers are dealt with by Nekola,[178] while Downie[179] describes an electronic device for identifying defects in heat-exchange equipment.

Reviewing sheet filtration applied to beer, Osgood[180] notes its extension to pre-filtration and polishing filtration of top and bottom beers, special

filter sheets being used for the latter; sterilizing sheets are available. Clarification procedures have received much attention, and Laneau[118] provides a critical discussion of the comparative results of the pulp filter, plate filter, centrifuge, and kieselguhr filter; he concludes that, in general, the pulp or kieselguhr filter serves best in large breweries, the plate filter or centrifuge being better for smaller plants, though two systems in conjunction may sometimes be desirable. The use of plate coolers and centrifuges for wort clarification is further discussed by Munder,[182] who deals also with the effectiveness of centrifuges for beer treatment. Filter-aid materials, the use of which has been discussed, include kieselguhr[183,184,185] and bentonite.[186]

Methods of studying the efficiency of bottling plant are examined critically by Rhodes[187]; Braems[188] deals with physical problems in bottling plant operation, recommending that filler nozzles should give a smooth flow, reaching well down into the bottle to give a short jet; they should preferably be non-emptying. The fundamental aim is to conserve the carbon dioxide equilibrium of the beer and minimize contact with air. An important study to determine acceptable specifications for beer bottles is being carried out in France, and recommendations are reported by Caron,[189] dealing with type of glass, colour, shape, capacity and the like, and the effects of temperature and pressure change. A somewhat similar American study of beer cartons is discussed by Nissen,[190] the tests applied (apart from measurement and physical inspection) including dropping, impact, and compression. The essentials of a fungicide for use with cork gaskets are considered by Berk,[191] who suggests that protein binders should be replaced by resins with which the fungicide (non-toxic to human beings) should be incorporated. Applications of plastics in the brewing industry[192] include use in pipe-lines, removable linings for metal drums, and binding for tiled floors.

Quaternary ammonium compounds as bottle-washing detergents are further described,[193,194] extension of their use to the sterilization of pipe-lines, fillers and other equipment in bottling stores being discussed, though they will not necessarily replace older detergents. Methods for studying detergent action have been devised by Bacon and Smith,[195] and Nekola[196] has investigated the more specific case of variations in detergent concentration in bottle-soaking tanks, showing how wastage may be avoided by controlled additions of the detergent (alkaline in this work) with proper mixing.

Instrumentation can be applied in the controlled treatment of brewery wastes,[197] and a matter worthy of serious consideration is that discussed in detail by Goldthorpe *et al.*[198]; it relates to the disposal of effluents containing synthetic detergents. Sewage works procedure in the past has been largely based on the use of soap as a detergent, but modern innovations raise a number of problems calling for much further work in their solution.

Patent specifications relating to brewing include: an attemperating device in which heating or cooling liquid passes through a coil of two tubular headers with connecting tubes forming a grid, the device being capable of rotation for cleaning[199]; a novel type of barrel with a collapsible inner lining into which beer can be passed and from which the beer is

removed by application of pressure through a side valve, thus avoiding contact with air and possible contamination[200] (*see also* de Clerck[55]); and a method for constructing casks in two layers of wood, the inner being less porous and resistant to internal pressure, and the outer more porous but better able to withstand rough usage.[201]

Analysis

A new method for testing the germinative capacity of seeds is based on the fact that peroxidase activity rapidly diminishes as germinative capacity is lost. Applied by Brücker[202] to old or heated barley, good agreement was found with standard germination tests, but bacterial action can lead to uncertain results in some cases. The density of barley and malt may be found by a volumenometer technique (Hagues and Russell),[203] and from a comparison of results from ground and unground samples the percentage air space in the grain can be calculated; of the malts examined, that with highest space content (20·6%) was very well modified and gave the best extract. A fundamental investigation of moisture content determination in barley and malt has been made by Trolle,[204] who adopts the principle that moisture is represented by the loss in weight undergone when a substance is heated to constant weight under conditions where reversible loss of moisture is the only significant change. The necessary conditions are fulfilled by drying the ground material *in vacuo* over phosphorus pentoxide at 40° c. until the weight is substantially constant. Adopting this as a reference method, other convenient routine methods can be standardized against it. A critical review of laboratory methods for moisture determination is also provided by Johnson.[205] Electric measurement of moisture in grain is discussed by Trionen,[206] and by Rasmussen and Anderson,[207] who describe a simplified instrument having a standard error of $\pm$ 0·36% over the range 10–17%.

The recently revised standard methods of malt analysis of the Institute of Brewing are critically reviewed by Comrie,[208] who suggests the need for collaborative testing of such methods and for further study of analytical methods applied to malt. Malt extract determination with special reference to the Congress method is discussed by Trolle,[209] while Hartong[210] describes his 'evaluation number' method of assessing the brewing value of malt, based on mashes carried out at 25, 45, 65 and 85° c. (or, in a simplified form, at 40 and 85° c. only); it is claimed that assessment at a single temperature is valueless, as it is necessary to examine both enzymic characters (lower temperatures) and the vulnerability to attack of the malt (higher temperatures). Kauert[211] discusses the assessment of malt quality in a general way. There are numerous references to amylase determination. Preece and Shadaksharaswamy[66,67] show that saccharification/time linearity for α-amylase conversions is only approximate even up to 10–15% conversion, whereas results in this range obtained by ferricyanide (standardized against maltose) are 25% greater than those obtained with Fehling's solution. Erlich and Burkert[212] find that aqueous extraction gives useful comparative results for a given cereal in α-amylase determination, but does not give complete extraction, for which purpose dilute salt solutions are to be preferred. Olson *et al.*[213]

have reached similar conclusions, and Bawden and Artis have compared[214] the efficiencies of different proteolytic enzyme preparations in facilitating the extraction of β-amylase from barley. Materials of widely different activity can be assayed for starch-converting power (dextrinization) by a method described in detail by de Becze *et al.*[215] involving starch conversion to the achromic point under standardized conditions. β-amylase determination is described by Noelting and Bernfeld.[216]

A specific gravity gradient tube prepared with bromobenzene and kerosene is well adapted for the examination of beers, worts and syrup solutions,[217] and can also be adapted to the determination of yeast concentration in suspensions[218]; the yeast cell itself contains 36·13% of solids.

Dextrin determination in wort and beer is critically discussed by van Roey[219] and an enzymic method for the purpose is proposed by de Clerck and van Roey.[220] Stone and Gray[221] point out the inadequacy of the classical methods for silica determination when applied to wort and beer, and propose a method employing ammonium molybdate and 1-amino-2-naphthol-4-sulphonic acid in presence of sulphite and bisulphite. A photometric method is also proposed for tannin, ferric ammonium citrate being added in presence of gum arabic and ammonia.[221] A full range of control blanks is needed in both methods. References to inorganic ions in beer include methods for fluorometric determination of aluminium,[222] and spectrographic analysis for tin and aluminium.[223]

The organoleptic testing of beer is of topical interest, and a valuable discussion of valid factors in the design of beer-tasting experiments is provided by Virden,[224] who emphasizes the importance of replication, independence of results, and reproducibility. Pairs tasting should be used with a panel as widely representative as possible of the beer-drinking public, whereas triangular tasting is best done by experts. Selection of one of two beers for drinking in canteen experiments may give useful information, but tasting and drinking tests do not necessarily give the same result. The influences of such variables as sample volume and the time interval between tasting tests are discussed by Slater and Frenkel.[225]

Colour determinations on wort and beer have been carried out spectrophotometrically by van Roey,[226] who expresses colour in terms of optical density at 400 mμ.; preliminary clarification of hazy samples is not necessary. Perhaps the most comprehensive contribution on the subject of colour is that of Hartong and van den Hoek[227] who discuss the application of tri-stimulus colorimetry and show that it can be used to give a valuable assessment of how the beer will appear to the consumer; the same workers describe a nephelometric method for determining beer haze, and show that the results can be correlated with those produced by adding small amounts of tannin. Colour compensation in turbidity measurements is eliminated in a photoelectric method applied to beer by Barnes and Stock.[228]

Industrial fermentations

Continuous mashing and flash conversion in the distillery production of alcohol from grain is outlined by Unger,[229] high-temperature cooking of raw grain being followed by rapid cooling to 63° c., contact with malt

slurry then giving 60–70% conversion to maltose in 2 minutes, with further active conversion during fermentation. Production of amylolytic liquor by submerged mould growth, allowing economies in the use of malt, is described by LeMense *et al.*[230] A systematic study of chemical changes during the maturation of whisky suggests the possibility of drawing up specifications for this material.[231] The production of light[232,233] and heavy[232,234] rums is discussed by Arroyo (*see also* idem.[235,236]); Gillaume,[237] considering the influence of raw materials and processing methods, suggests the introduction in France of official methods of analysis to control rum imports. According to Barbet[238] vacuum distilled brandy is of finer quality than that distilled at ordinary pressure owing to improved removal of aldehydes and fusel oil; rectification problems are also dealt with by Mariller.[239]

Processes covered by patent specifications relating to alcohol production include: a continuous fermentation process with re-cycling of vinasse[240]; recovery of alcohol from fermentation carbon dioxide[241]; clarification of fermented liquors[242]; concentration of distillery slop[243]; drying apparatus for slop[244]; and the preparation of wood for use in ageing spirituous liquors.[245] A method for glycerol production has been described.[246] Description has been given of a number of raw materials for industrial fermentations, together with their characters and preparation for use: they include bisulphite lyes[247] (for ethyl alcohol), wood liquors,[248] and molasses.[249]

In the case of Californian wines, no correlation exists between the age of a finished wine and its redox potential, this character being more closely related to the previous treatment[250]; dehydration products of fructose occur in baked Californian wines.[251] Numerous varieties of grapes have been tested as to their suitability for red wines of Venice,[252] and the characters of Spanish sherries have been surveyed[253]; the differences between these sherries and those of California are due to the use of flor yeast and the solero system in Spain and the practice of baking in California. Garino-Canino[254] notes improvement in the organoleptic qualities of wines from grapes previously treated with carbon dioxide; the malic acid content of the must appears to be diminished and colouring matters undergo favourable changes. Enzymic and non-enzymic factors both contribute to the darkening of white wines.[255] Winery sanitation is discussed by Vaughn,[256] and Gentilini[257] presents a critical survey of sulphite removal from musts; in order of efficiency the simplest methods are: air blowing, stirring, and single-jet decanting. Maass[258] treats of the significance of pectase in musts, and Kielhöfer[259] describes the factors concerned in the fining of wine by tylose (methyl cellulose); the process of blue-fining with ferricyanide is only necessary when the total concentration of copper and iron exceeds 3 p.p.m.[260] Reduction of the possibility of secondary fermentation in sweet light wines is achieved by sterilizing the containers, maintaining alcohol above 14%, by using at least 200 p.p.m. of sulphur dioxide, and by adding sulphur dioxide in frequent small doses.[261] Tartrate recovery from pomace has been investigated[262] and a method of extraction patented.[263]

Methods for the manufacture of vinegar have been protected,[264,265] and Böhme[266] describes two German vinegar substitutes based on formic acid.

The *Aerobacillus polymyxa* fermentation of wheat mashes with production of butane-2 : 3-diol has undergone further study. On a pilot-plant scale, the fermented mash has been distilled to remove ethanol, screened and concentrated, and the diol removed by steam-stripping and recovered by rectification; daily output figures are given.[267] Barley can be used instead of wheat if the process is slightly modified.[268] With wheat, a fermentation efficiency of 90% can be attained, but the frequent use of freshly cultured material or improved strains is desirable.[269] Further study of the conditions for diol production with *A. aerogenes* is provided by Olson and Johnson,[270] while processes described for recovery include one involving dialysis and base-exchange treatment[271] and one in which the liquor is extracted with acetone after lime treatment to remove sludge.[272]

Nilsson[273] discusses the possibilities of production of calcium lactate in dairies, using a mixed culture of *Lactobacillus* spp. and a mycoderma, and Engel[274] describes a process yielding a product from a mixture of whey, yeast culture and sucrose that can be used as a beverage or for flavouring ice cream. Other uses of whey have been described elsewhere.[173] The difficulties inherent in the use of cane molasses for the fermentative production of citric acid are reviewed by Oxford,[275] and a culture medium claimed to give a 90–92% yield of citric acid when fermented with *Aspergillus niger* has been protected[276]; another process is that of Waksman.[277] Fermentation of gaseous hydrocarbons such as methane, ethane and propane with *Bacillus paraffinicus* yields fatty acids, esters and low-boiling-point alcohols[278]; heavy metal salts and phosphates are required in the aqueous medium. Fermentation of a mixture containing sugar, urea and nutrient salts with *Acetobacter suboxydans* following the action of *Aerobacter* sp. gives improved yields of 3-hydroxybutan-2-one,[279] and various carbohydrates can be converted to 1-ketoglutaric-(propan-1-one-1 : 3-dicarboxylic) acid by fermentation with *Pseudomonas* spp.

References

1 *See* e.g. *J. Inst. Brew.*, **1949**, 189
2 Ibid., 196
3 Ibid., 261
4 M.B.A.A. Commun., Nov.–Dec., 1948; *J. Inst. Brew.*, **1949**, 60
5 *See J. Inst. Brew.*, **1949**, 336
6 Ibid., 1
7 Wright, E. P., ibid., 351
8 Slight, A. M., ibid., 223
9 Hunter, H., *Proc. tech. Sess. Amer. Soc. Brew. Chem.*, **1947**, 8
10 Idem, *Farming*, March, 1949; *J. Inst. Brew.*, **1949**, 321
11 Earnshaw, F., Recommended Varieties of Wheat and Barley, N.I.A.B., 1948
12 "Cereal Seed" (London: Inst. Corn & Agric. Merchants and Nat. Assoc. Corn & Agric. Merchants, 1949)
13 Mid-West Barley Improvement Assoc., U.S.A.; *J. Inst. Brew.*, **1949**, 194, 337
14 Hardy, E. A., Barley Improvement Inst. Bull., No. 1, 1949
15 Moore, H. I., *Agriculture, London*, 1949, **56**, 314; *J. Inst. Brew.*, **1949**, 336
16 Pinon, H., *C.R. Acad. Sci., Paris*, 1949, **224**, 1852
17 Pulkki, L. H. and Puutula, K., *Acta chem. scand.*, 1948, **2**, 461
18 Robinson, A. D., Lynd, L. E. and Miles, B. J., *Canad. J. Res.*, 1948, **26B**, 711; *J. Inst. Brew.*, **1949**, 117
19 Zeleny, L., *Trans. Amer. Ass. Cereal Chem.*, 1948, **6**, 112

[20] McElroy, L. W., Clandinin, D. R., Lobay, W. and Pethybridge, S. E., *J. Nutrit.*, 1949, **37**, 329
[21] Bishop, L. R., *J. Inst. Brew.*, **1930**, 336
[22] Vintner, R. A., *Agriculture, London*, 1949, **55**, 488 ; *J. Inst. Brew.*, **1949**, 116
[23] Hayles, W. A., *Agriculture, London*, 1949, **56**, 228 ; *J. Inst. Brew.*, **1949**, 387
[24] Jolley, F. R., *J. Inst. Brew.*, **1949**, 343
[25] Gilman, J. G. and Semenink, G., *Trans. Amer. Ass. Cereal Chem.*, 1948, **6**, 108
[26] Carr, J. B. and Hadley, C. G., B.P. 606,588
[27] Parkin, E. A., *Ann. appl. Biol.*, 1946, **33**, 97
[28] Woodward, R. C., Mackay, I. A. and I.C.I. Ltd., B.P. 607,564
[29] Trehan, K. N. and Pingle, S. V., *Indian Farming*, 1947, **8**, 404
[30] Price, M. D., *J. Inst. Brew.*, **1948**, 213
[31] Barton, M. V. and Solt, M. L., *Contr. Boyce Thompson Inst.*, 1948, **15**, 259
[32] Templeman, W. G. and Sexton, W. A., *Proc. roy. Soc.*, 1946 [B], **133**, 300
[33] Dickson, A. D., Shands, H. L. and Burkhart, B. A., *Cereal Chem.*, 1949, **26**, 13 ; *J. Inst. Brew.*, **1949**, 177
[34] Sandegren, E., *J. Inst. Brew.*, **1948**, 200
[35] Cherry-Downes, H. A. D., ibid., 208
[36] Roby Ltd., R. and Wesson, J. P., B.P. 608,791–2 and 609,332 ; *J. Inst. Brew.*, **1949**, 257
[37] Zunterer, K., *Brauwelt*, **1948A**, 461
[38] Wilkinson, E. H., *Agriculture, London*, 1949, **56**, 160 ; *J. Inst. Brew.*, **1949**, 263
[39] Salmon, E. S., *J. Inst. Brew.*, **1949**, 29
[40] Keyworth, W. G., *A.R.E. Malling Res. Sta.*, **1946**, 157
[41] Salmon, E. S., *J. Inst. Brew.*, **1949**, 234
[42] Fletcher, L., ibid., 369
[43] Keyworth, W. G. and Hitchcock, M. M., *A.R.E. Malling Res. Sta.*, **1947**, 148 ; *J. Inst. Brew.*, **1949**, 62
[44] Keyworth, W. G., *J. hort. Sci.*, 1948, **24**, 149
[45] Tolhurst, J. A. H., *A.R. agric. hort. Res. Sta., Bristol*, **1946**, 105
[46] Keyworth, W. G. and Hitchcock, M. M., *A.R.E.Malling Res. Sta.*, **1947**, 150; *J. Inst. Brew.*, **1949**, 62
[47] Keyworth, W. G., *A.R.E. Malling Res. Sta.*, **1946**, 142
[48] Hoerner, G. R., *Brewers Digest*, Apr., 1949, 45 ; *J. Inst. Brew.*, **1949**, 243
[49] Lambert, J. G., *Rev. Int. Brass. Malt.*, Jan.–Feb., 1948, 1 ; *J. Inst. Brew.*, **1949**, 48
[50] Verzele, M. and Eugene, P., *Fermentatio*, **1948** (x–xii), 95 ; *J. Inst. Brew.*, **1949**, 243
[51] Goedkoop, W., *Brewers Digest*, Sept., 1948, 50 ; *J. Inst. Brew.*, **1949**, 48
[52] Siegfried, H., *Schweiz. Brau.-Runds.*, 1946, **57**, 35
[53] Kolbach, P., ibid., 1948, **59**, 71 ; *J. Inst. Brew.*, **1949**, 243
[54] Govaert, F., *J. Inst. Brew.*, **1949**, 175
[55] de Clerck, J., ibid., 291
[56] Richardson, F. N., ibid., 96
[57] Myer, S., ibid., 199, 265
[58] May, H. L. A., *J. Inc. Brewers Guild*, 1949, **35**, 452
[59] Lampitt, L. H., Fuller, C. H. F. and Goldenberg, N., *J. Soc. Chem. Ind.*, 1948; **67**, 38, 41, 97, 121
[60] Lampitt, L. H., Fuller, C. H. F., Goldenberg, N. and Green, G. H., ibid., 178
[61] Rooke, H. S., Lampitt, L. H. and Jackson, E. M., *Biochem. J.*, 1949, **45**, 231 ; *J. Inst. Brew.*, **1949**, 401
[62] le Corvaisier, H., *Bull. Soc. Chim. biol.*, 1948, **30**, 202 ; *J. Inst. Brew.*, **1949**, 185
[63] Idem, *J. Inst. Brew.*, **1949**, 237
[64] Myrbäck, K., *Wallerstein Lab. Commun.*, 1948, **11**, 209 ; *J. Inst. Brew.*, **1949**, 54
[65] Bourne, E. J., Haworth, W. N., Macey, A. and Peat, S., *J. chem. Soc.*, **1948**, 924 ; *J. Inst. Brew.*, **1948**, 340
[66] Preece, I. A. and Shadaksharaswamy, M., *Biochem. J.*, 1949, **44**, 270 ; *J. Inst. Brew.*, **1949**, 253
[67] Idem, *J. Inst. Brew.*, **1949**, 103, 298, 373
[68] Mindell, F. M., Agnew, A. L. and Caldwell, M. L., *J. Amer. chem. Soc.*, 1949, **71**, 1779 ; *J. Inst. Brew.*, **1949**, 333
[69] Montgomery, E. M., Weakley, F. B. and Hilbert, G. E., *J. Amer. chem. Soc.*, 1949, **71**, 1682 ; *J. Inst. Brew.*, **1949**, 333

[70] Wolfrom, M. L., Georges, L. W., Thompson, A., and Miller, I. L., *J. Amer. chem. Soc.*, 1949, **71**, 2873 ; *J. Inst. Brew.*, **1949**, 404
[71] Sugihara, J. M. and Wolfrom, M. L., *J. Amer. chem. Soc.*, 1949, **71**, 3357
[72] Blom, J. and Schwarz, B., *J. Inst. Brew.*, **1949**, 240
[73] Tsuchiya, H. M., Montgomery, E. M. and Corman, J., *J. Amer. chem. Soc.*, 1949, **71**, 3265 ; *J. Inst. Brew.*, **1949**, 404
[74] Kneen, E. and Spoerl, J. M., *Proc. tech. Sess. Amer. Soc. Brew. Chem.*, 1948, 20 ; *J. Inst. Brew.*, **1949**, 186
[75] Witt, P. R. and Ohle, R. L., *Proc. tech. Sess. Amer. Soc. Brew. Chem.*, 1948, 28 ; *J. Inst. Brew.*, **1949**, 186
[76] Owen, W. L., junr., and Owen, W. L., U.S.P. 2,392,258
[77] Haworth, W. N. and Stacey, M., B.P. 618,999
[78] French, D., Levine, M. L., Pazur, J. H. and Norberg, E., *J. Amer. chem. Soc.*, 1949, **71**, 353 ; *J. Inst. Brew.*, **1949**, 255
[79] Danielsson, C. E., *Biochem. J.*, 1949, **44**, 387 ; *J. Inst. Brew.*, **1949**, 321
[80] Maestenbroek, G., *Bull. Assoc. anc. Etud., Louvain*, 1949, **45**, 1 ; *J. Inst. Brew.*, **1949**, 405
[81] Thuman, W. C., Brown, A. G. and McBain, J. W., *J. Amer. chem. Soc.*, 1949, **71**, 3129 ; *J. Inst. Brew.*, **1949**, 405
[82] Bishop, L. R., R.I.C. Symposium, St. Andrews, 1949 ; *J. Inc. Brewers Guild*, 1949, **35**, 440
[83] Idem, *J. Inst. Brew.*, **1949**, 147
[84] Hopkins, R. H. and Berridge, N. J., ibid, 306
[85] St. Johnston, J. H., ibid., **1948**, 305
[86] Bonot, A., *Bull. Soc. Chim. biol., Paris*, 1946, **28**, 852
[87] Danielsson, C. E. and Sandegren, E., *Acta chim. scand.*, 1947, **1**, 917
[88] Lundin, H., *Brewers Digest*, Oct., 1948, 55 ; *J. Inst. Brew.*, **1949**, 47
[89] Schwimmer, S. and Balls, A. K., *J. biol. Chem.*, 1948, **176**, 465 ; *J. Inst. Brew.*, **1949**, 332
[90] Cruess, W. V. and Kilbuck, J., *Rev. Quim. industr., B. Aires*, 1948, **17**, No. 189, 22
[91] Beaven, G. H. and Brown, F., *Biochem. J.*, 1949, **45**, 221 ; *J. Inst. Brew.*, **1949**, 405
[92] Wallerstein, J. S., Hale, M. G. and Alba, R. T., *Wallerstein Lab. Commun.*, 1948, **11**, 281 ; *J. Inst. Brew.*, **1949**, 47
[93] Idem, ibid., 319 ; ibid., 117
[94] Barker, S. A., Bourne, E. J. and Peat, S., *J. chem. Soc.*, **1949**, 1705 ; *J. Inst. Brew.*, **1949**, 403
[95] Idem, *J. chem. Soc.*, **1949**, 1712 ; *J. Inst. Brew.*, **1949**, 403
[96] Bourne, E. J., Sitch, D. A. and Peat, S., ibid., 1448 ; ibid., 402
[97] Hestrin, S., *Wallerstein Lab. Commun.*, 1948, **11**, 193 ; *J. Inst. Brew.*, **1949**, 50
[98] Gottschalk, A., ibid., 1949, **12**, 55 ; ibid., 249
[99] Hestrin, S., ibid., 45 ; ibid., 250
[100] Suomalainen, H. and Towonen, T., *Arch. Biochem.*, 1948, **18**, 109
[101] Gottschalk, A., *Wallerstein Lab. Commun.*, 1947, **10**, 109 ; *J. Inst. Brew.*, **1947**, 318
[102] Federico, L., *Ann. chim. appl., Roma*, 1948, **38**, 619
[103] Boinot, F., *Indust. agric. aliment.*, 1948, **65**, 279
[104] Wilkinson, J. F., *Biochem. J.*, 1949, **44**, 460 ; *J. Inst. Brew.*, **1949**, 325
[105] Kiessling, A., *Industr. agric. aliment.*, 1949, **66**, 111
[106] Spencer, E. Y., Robinson, A. D., McElroy, L. W. and Kastelic, J., *Canad. J. Res.*, 1949, **27F**, 194 ; *J. Inst. Brew.*, **194**, 325
[107] Meade, R. E., Pollard, H. L. and Rodgers, N. E., Assrs. to Western Condensing Co., U.S.P. 2,433,063–4 and 2,433,232
[108] *Cf.* Pollard, H. L., Rodgers, N. E. and Meade, R. E., Assrs. to Western Condensing Co., U.S.P. 2,449,140–3
[109] *Cf.* Rodgers, N. E., Pollard, H. L. and Meade, R. E., Assrs. to Western Condensing Co., U.S.P. 2,449,144
[110] Tanner, junr., F. W. and van Lanen, J. M., Assrs. to U.S.A., U.S.P. 2,449,340
[111] Novak, A. F., Assr. to J. E. Seagram & Sons, Inc., U.S.P. 2,447,814
[112] Levine, H., Oyaas, J. E., Wasserman, L., Hoogerheide, J. C. and Stern, R. M., *Ind. Eng. Chem.*, 1949, **41**, 1665 ; *J. Inst. Brew.*, **1949**, 393
[113] Atkin, L., *Wallerstein Lab. Commun.*, 1949, **12**, 141 ; *J. Inst. Brew.*, **1949**, 326
[114] Duraiswami, S. and Subramaniam, M. K., *J. Ind. Sci. Res., India*, 1948, **7B**, 129

[115] Phaff, H. J. and Mrak, E. M., *Wallerstein Lab. Commun.*, 1948, **11**, 261 ; 1949, **12**, 29 ; *J. Inst. Brew.*, **1949**, 120, 248
[116] Winge, O. and Roberts, C., *C.R. Lab. Carlsberg, Ser. physiol.*, 1949, **24**, 241 ; *J. Inst. Brew.*, **1949**, 249
[117] Bouthilet, R. J., Neilson, N. E., Mrak, E. M. and Phaff, H. J., *J. gen. Microbiol.*, 1949, **3**, 282 ; *J. Inst. Brew.*, **1949**, 326
[118] Stewart, L. C., Richtmyer, N. K. and Hudson, C. S., *J. Amer. chem. Soc.*, 1949, **71**, 2277 ; *J. Inst. Brew.*, **1949**, 327
[119] Mueller, E., *Amer. Brewer*, Feb., 1949, 54 ; *J. Inst. Brew.*, **1949**, 248
[120] Laufer, S. and Mohr, H., *Proc. tech. Sess. Amer. Soc. Brew. Chem.*, 1948, 58 ; *J. Inst. Brew.*, **1949**, 180
[121] Atkin, L., Gray, P. P., Moses, W. and Feinstein, M., *Wallerstein Lab. Commun.*, 1949, **12**, 153 ; *J. Inst. Brew.*, **1949**, 327
[122] Clark, W. M., *Amer. Brewer*, Dec., 1948 (i), 25 ; *J. Inst. Brew.*, **1949**, 121
[123] van Lanen, J. M., LeMense, E. H., Anellis, A. and Corman, J., *Cereal Chem.*, 1948, **25**, 326 ; *J. Inst. Brew.*, **1949**, 121
[124] Thorne, R. S. W., *J. Inst. Brew.*, **1949**, 18
[125] Damlé, W. R. and Thorne, R. S. W., ibid., 13
[126] Taylor, E. S., *J. gen. Microbiol.*, 1949, **3**, 211 ; *J. Inst. Brew.*, **1949**, 326
[127] Thorne, R. S. W., *J. Inst. Brew.*, **1949**, 201
[128] Barton-Wright, E. C. and Thorne, R. S. W., *ibid.*, 383
[129] Schmidt, E., *Angew. Chem.*, 1947, **59A**, 16
[130] Floro, M. B., Williams, V., Flook, W. A. and Collier, J. S., *Int. Sug. J.*, 1948, **50**, 234
[131] Vasquez, E. A., *Bol. Off. Asoc. Tecn. Azuc.*, 1948, **7**, 39
[132] Harris, E. E., Hannan, M. L. and Marquardt, R. R., *Ind. Eng. Chem.*, 1948, **40**, 2068 ; *J. Inst. Brew.*, **1949**, 180
[133] Johnson, M. C. and Harris, E. E., *J. Amer. chem. Soc.*, 1948, **70**, 2961 ; *J. Inst. Brew.*, **1949**, 52
[134] Singh, K., Agarwal, P. N. and Peterson, W. H., *Arch. Biochem.*, 1948, **18**, 181
[135] Bunker, H. J., *Chem. & Ind.*, **1948**, 179
[136] Zagrodzki, S., *Przem. chem.*, 1948, **27**, 401
[137] Myers, R. P. and Speck, M. L., Assrs. to Nat. Dairy Res. Labs., Inc., U.S.P. 2,448,680
[138] Braude, R., *Chem. & Ind.*, **1948**, 259
[139] van Laer, M. H., *Chim. et Industr.*, 1948, **60**, 94 ; *J. Inst. Brew.*, **1949**, 51
[140] Shimwell, J. L., *J. Inst. Brew.*, **1949**, 26
[141] Kulka, D., Cosbie, A. J. C. and Walker, T. K., ibid., 315
[142] Kulka, D., Preston, J. M. and Walker, T. K., ibid., 141
[143] Brown, B. M., Barton-Wright, E. C. and Lyon, A. I. L., ibid., 100
[144] Helm, E., Reprint, *Schweiz. Brau.-Runds.*, Special Congress No., 1949 ; *J. Inst. Brew.*, **1949**, 328
[145] Shimwell, J. L., *Wallerstein Lab. Commun.*, 1949, **12**, 71, 187 ; *J. Inst. Brew.*, **1949**, 251, 328
[146] Walker, T. K. and Kulka, D., ibid., 7 ; ibid., 250
[147] Olshausen, J. J., *Proc. tech. Sess. Amer. Soc. Brew. Chem.*, 1947, 63
[148] Chevalier, P., *Brasserie*, 1949, **3**, 119 ; *J. Inst. Brew.*, **1949**, 327
[149] Plumpton, M. W., *J. Inst. Brew.*, **1949**, 278
[150] Seng, G. W., *Brewers Digest*, May, 1949, 43 ; *J. Inst. Brew.*, **1949**, 329
[151] Chabot, E., *Fermentatio*, 1949 (i), 1 ; *J. Inst. Brew.*, **1949**, 330
[152] Luers, H., *Brewers Digest*, May, 1949, 39 ; *J. Inst. Brew.*, **1949**, 330
[153] Idem, ibid., Sept., 1948, 45 ; *J. Inst. Brew.*, **1949**, 51
[154] de Clerck, J., *Rev. Int. Brass. Malt.*, 1948 (iii–iv), 35 ; *J. Inst. Brew.*, **1949**, 52
[155] Smith, junr., A. C., *Amer. Brewer*, Feb., 1949, 19 ; *J. Inst. Brew.*, **1949**, 252
[156] Rippel, K., *Brauwissenschaft*, 1948, No. 3 ; *J. Inst. Brew.*, **1949**, 122
[157] Urion, E., *Brasserie*, 1949, **3**, 140 ; *J. Inst. Brew.*, **1949**, 395
[158] Schild, E. and Hugmann, M. V., *Brewers Digest*, June, 1949, 43 ; *J. Inst. Brew.*, **1949**, 396
[159] van Roey, M. G., *Bull. Assoc. anc. Etud., Louvain*, 1949, **45**, 53 ; *J. Inst. Brew.*, **1949**, 396
[160] Urion, E. and Lejeune, G., *Brasserie*, 1949, **3**, 148 ; *J. Inst. Brew.*, **1949**, 397
[161] Hartong, B. D., *Rev. Int. Brass. Malt.*, 1948 (iii–iv), 25 ; *J. Inst. Brew.*, **1949**, 53

[162] de Rijck, M., *Pet. J. Brass.*, 1948, **56**, 873 ; *J. Inst. Brew.*, **1949**, 54

[163] Beattie, G. B., *Bottling*, July, 1949, 20 ; *J. Inst. Brew.*, **1949**, 330

[164] Becker, K., *Brewers Digest*, Jan., 1949, 37 ; Feb., 1949, 43 ; *J. Inst. Brew.*, **1949**, 181

[165] Hagues, G., *J. Inst. Brew.*, **1949**, 113

[166] Scott, J. W., ibid., 38

[167] Moortgat, E., *Bull. Assoc. anc. Etud., Louvain*, 1949, **45**, 65 ; *J. Inst. Brew.*, **1949**, 395

[168] Watkins, W. J., *J. Inst. Brew.*, **1948**, 295

[169] Wiles, A. E., ibid., **1949**, 165, 172

[170] Anon., *Brew. Guard.*, 1948, **77**, 19

[171] Ernst, J., *Brauwelt*, 1948**A**, 337

[172] Klein, A. A., U.S.P. 2,440,276

[173] *See* e.g. *J. Inst. Brew.*, **1949**, 7

[174] Zunterer, G. K., *Brauwelt*, 1948**A**, 347

[175] Young, R. S., *J. Inst. Brew.*, **1949**, 371

[176] Smith, U. W., *Amer. Brewer*, Oct., 1948, 21 ; *J. Inst. Brew.*, **1949**, 123

[177] Bergmann, J. H., *Amer. Brewer*, Aug., 1949, 19 ; *J. Inst. Brew.*, **1949**, 397

[178] Nekola, W., *Amer. Brewer*, Nov., 1948, 24 ; *J. Inst. Brew.*, **1949**, 123

[179] Downie, C. C., *Brewers J.*, 1948, **84**, 502 ; *J. Inst. Brew.*, **1949**, 54

[180] Osgood, C., *Bottler & Packer*, 1949, **23** (i), 46 ; (ii), 44

[181] Laneau, R., *Bull. Assoc. anc. Etud., Louvain*, 1948, **44**, 153 ; *J. Inst. Brew.*, **1949**, 182

[182] Munder, H., *Brauwelt*, 1948, 533

[183] Moll, A., *Schweiz. Brau.-Runds.*, 1949, **60**, 143 ; *J. Inst. Brew.*, **1949**, 398

[184] Lambert, J. G., *Pet. J. Brass.*, 1948, **56**, 814 ; *J. Inst. Brew.*, **1949**, 52

[185] Horine, F. L., *Brewers Digest*, Nov., 1948, 43 ; *J. Inst. Brew.*, **1949**, 123

[186] Lynch, C., *Chim. et Industr.*, 1949, **61**, 189 ; *J. Inst. Brew.*, **1949**, 184

[187] Rhodes, N. G., *Amer. Brewer*, Dec., 1948 (i), 46 ; *J. Inst. Brew.*, **1949**, 122

[188] Braems, J., *Bull. Assoc. anc. Etud., Louvain*, 1949, **45**, 23 ; *J. Inst. Brew.*, **1949**, 331

[189] Caron, P.-A., *Brasserie*, 1949, **3**, 170, 190 ; *J. Inst. Brew.*, **1949**, 398

[190] Nissen, B. H., *Proc. tech. Sess. Amer. Soc. Brew. Chem.*, 1948, 95; *J. Inst. Brew.*, **1949**, 184

[191] Berk, S., *Ind. Eng. Chem.*, 1949, **41**, 627 ; *J. Inst. Brew.*, **1949**, 184

[192] Jaray, F. F., *J. Inc. Brewers Guild*, 1949, **35**, 257 ; *J. Inst. Brew.*, **1949**, 332

[193] Resuggan, J. C. L., *Bottling*, Jan., 1949, 38 ; *J. Inst. Brew.*, **1949**, 183

[194] Idem, *Bottling*, Oct., 1949, 46 ; *J. Inst. Brew.*, **1949**, 398

[195] Bacon, O. C. and Smith, J. E., *Ind. Eng. Chem.*, 1948, **40**, 2361 ; *J. Inst. Brew.*, **1949**, 122

[196] Nekola, W., *Brewers Digest*, Nov., 1948, 45 ; *J. Inst. Brew.*, **1949**, 183

[197] Pearson, A. O., *Brewers Digest*, Feb., 1949, 47 ; *J. Inst. Brew.*, **1949**, 253

[198] Goldthorpe, H. H., Hillier, W. H., Lumb, C. and Lawrence, A. S. C., *Chem. & Ind.*, 1949, 679 ; *J. Inst. Brew.*, **1949**, 399

[199] Aluminium Plant & Vessel Co. Ltd. and Paine, S. W. T., B.P. 608,972 ; *J. Inst. Brew.*, **1949**, 257

[200] Leperre, J. E. L., B.P. 615,258

[201] Roberts, E., B.P. 608,838 ; *J. Inst. Brew.*, **1949**, 257

[202] Brücker, H., *Physiol. plantarum*, 1948, **1**, 343 ; *J. Inst. Brew.*, **1949**, 243

[203] Hagues, G. and Russell, J., *J. Inst. Brew.*, **1949**, 110

[204] Trolle, B., ibid., 354

[205] Johnson, A. S., *Chem. & Ind.*, **1949**, 511

[206] Trioen, *Pet. J. Brass.*, 1948, **56**, 980 ; *J. Inst. Brew.*, **1949**, 118

[207] Rasmussen, H. E. and Anderson, J. A., *Canad. J. Res.*, 1949, **27F**, 249 ; *J. Inst. Brew.*, **1949**, 324

[208] Comrie, A. A. D., *J. Inst. Brew.*, **1949**, 274

[209] Trolle, B., *Wallerstein Lab. Commun.*, 1949, **12**, 127 ; *J. Inst. Brew.*, **1949**, 322

[210] Hartong, B. D., *Amer. Brewer*, June, 1949, 19 ; *J. Inst. Brew.*, **1949**, 389

[211] Kauert, G., *Fementatio*, 1949 (ii), 17 ; *J. Inst. Brew.*, **1949**, 388

[212] Erlich, V. L. and Burkert, G. M., *Cereal Chem.*, 1949, **26**, 326 ; *J. Inst. Brew.*, **1949**, 389

[213] Olson, W. J., Lowry, M. T. and Dickson, A. D., *Proc. tech. Sess. Amer. Soc. Brew. Chem.*, 1948, 13 ; *J. Inst. Brew.*, **1949**, 177

[214] Bawden, R. F. and Artis, G., ibid., 1 ; ibid., 177

[215] de Beeze, G. I., Votaw, junr., J. W. and Nanz, R. H., *Cereal Chem.*, 1949, **26**, 148; *J. Inst. Brew.*, **1949**, 245
[216] Noelting, G. and Bernfeld, P., *Helv. chim. Acta*, 1948, **31**, 286; *J. Inst. Brew.*, **1949**, 49
[217] Atkin, L., Stone, I. and Gray, P. P., *Wallerstein Lab. Commun.*, 1948, **11**, 281; *J. Inst. Brew.*, **1949**, 117
[218] Atkin, L., Feinstein, M. and Gray, P. P., ibid., 289; ibid., 120
[219] van Roey, G., *Chim. et Industr.*, 1948, **60**, 94; *J. Inst. Brew.*, **1949**, 49
[220] de Clerck, J. and van Roey, G., *Bull. Assoc. anc. Etud., Louvain*, 1948, **44**, 105; *J. Inst. Brew.*, **1949**, 118
[221] Stone, I. and Gray, P. P., *Wallerstein Lab. Commun.*, 1948, **11**, 301; *J. Inst. Brew.*, **1949**, 118
[222] Tullo, J. W., Stringer, W. J. and Harrison, G. A. F., *Analyst*, 1949, **74**, 296; *J. Inst. Brew.*, **1949**, 392
[223] Alexander, O. R. and Biske, V. M., *Proc. tech. Sess. Amer. Soc. Brew. Chem.*, 1948, 69; *J. Inst. Brew.*, **1949**, 179
[224] Virden, C. J., *J. Inst. Brew.*, **1949**, 228
[225] Slater, R. R. and Frenkel, G. K., *Proc. tech. Sess. Amer. Soc. Brew. Chem.*, 1948, 106; *J. Inst. Brew.*, **1949**, 182
[226] van Roey, G., *Bull. Assoc. anc. Etud., Louvain*, 1949, **45**, 16; *J. Inst. Brew.*, **1949**, 331
[227] Hartong, B. D. and van den Hoek, A. P., *J. Inst. Brew.*, **1949**, 156
[228] Barnes, R. B. and Stock, C. R., *Analyt. Chem.*, 1949, **21**, 181; *J. Inst. Brew.*, **1949**, 252
[229] Unger, E. D., *Amer. Brewer*, Sept., 1948, 21; *J. Inst. Brew.*, **1949**, 47
[230] LeMense, E. H., Sohns, V. E., Corman, J., Blom, R. H., van Lanen, J. M. and Langlykke, A. F., *Ind. Eng. Chem.*, 1949, **41**, 100; *J. Inst. Brew.*, **1949**, 181
[231] Liebmann, A. J. and Scherl, B., *Ind. Eng. Chem.*, 1949, **41**, 534
[232] Arroyo, R., *Int. Sug. J.*, 1948, **50**, 289
[233] Idem, ibid., 150
[234] Idem, U.S.P. 2,386,924
[235] Idem, *Sugar*, 1949, **44** (vii), 34
[236] Idem, *Int. Sug. J.*, 1949, **51**, 163
[237] Gillaume, J., *Industr. agric. aliment.*, 1948, **65**, 309
[238] Barbet, E., ibid., 291
[239] Mariller, C., ibid., 287
[240] Boeckeler, B. C., Assr. to Chemprotin Products, U.S.P. 2,440,925
[241] Akties. Dansk Gaerings-Industri, B.P. 610,341; *J. Inst. Brew.*, **1949**, 257
[242] Cornwall, R. T. K. and Porter, D. S., Assrs. to Amer. Viscose Co., U.S.P. 2,437,939
[243] Pattee, E. C., Assr. to Nat. Distillers Products Corp., U.S.P. 2,391,918
[244] Maglaughlin, J. W., U.S.P. 2,440,778
[245] Krebs, E. T., B.P. 621,487
[246] Fulmer, E. I., Underkofler, L. A. and Hickey, R. J., Assrs. to Iowa State Coll. Res. Found., U.S.P. 2,388,840
[247] Alexa, G. and Saveanu, *Bull. Ecole Polyt. Jassey*, 1948 (i), **3**, 435
[248] Hall, H. E. and Coleman, L. C., Assrs. to Masonite Corp., U.S.P. 2,444,823
[249] Sattler, L. and Zerban, F. W., *Ind. Eng. Chem.*, 1949, **41**, 1401; *J. Inst. Brew.* **1949**, 325
[250] Joslyn, M. A., *Ind. Eng. Chem.*, 1949, **41**, 587
[251] Amerine, M. A., *Food Res.*, 1948, **13**, 264
[252] Cosmo, I., *Ann. Sper. agr.*, 1948, **2**, 201
[253] Brajnikoff, I. and Cruess, W. V., *Food. Res.*, 1948, **13**, 128
[254] Garino-Canino, E., *Ann. Sper. agr.*, 1949, **3**, 343
[255] Cruess, W. V., *Fruit Prod. J.*, 1948, **28**, 4
[256] Vaughn, R. H., ibid., 1949, **28**, 266
[257] Gentilini, L., *Ann. Sper. agr.*, 1949, **3**, 351
[258] Maass, H., *Dtsch. Lebensmitt. Rdsch.*, 1948, **44**, 257
[259] Kielhöfer, E., *Z. Lebensmitt. Untersuch. Forsch.*, 1948, **88**, 76
[260] Fessler, J. H., *Fruit Prod. J.*, 1949, **28**, 167
[261] Yang, H. Y. and Wiegand, E. H., ibid., 134
[262] Legault, R. R., Nimmo, C. C., Hendel, C. E. and Notter, G. K., *Ind. Eng. Chem.*, 1949, **41**, 466

[263] Metzner, E. K., U.S.P. 2,440,907
[264] Silbernagel, F. C., Assr. to A. M. Richter Sons Inc., U.S.P. 2,395,510
[265] Krebel, E. J. B., U.S.P. 2,390,717
[266] Böhme, H., *Dtsch. Lebensmitt. Rdsch.*, 1948, **44**, 126
[267] Wheat, J. A., Leslie, J. D., Tomkins, R. V., Mitton, H. E., Scott, D. S. and Ledingham, G. A., *Canad. J. Res.*, 1948, **26F**, 469
[268] Tomkins, R. V., Scott, D. S. and Simpson, J. F., ibid., 497
[269] Blackwood, A. C., Wheat, J. A., Leslie, J. D., Ledingham, G. A. and Simpson, J. F., ibid., 1949, **27F**, 199
[270] Olson, B. H. and Johnson, M. J., *J. Bact.*, 1948, **55**, 209
[271] Cornwall, R. T. K., Assr. to Sylvania Ind. Corp., U.S.P. 2,390,779
[272] Liebmann, A. J. and de Becze, G., Assrs. to Schenley Distillers Corp., U.S.P. 2,389,263
[273] Nilsson, G., Svenska Mejeritidn., 1948, **40**, 207
[274] Engel, E. R., U.S.P. 2,449,064
[275] Oxford, A. E., *S. Afr. industr. Chem.*, 1949, **3**, 50
[276] Szucs, J., U.S.P. 2,438,136
[277] Waksman, S. A., Assr. to Merck & Co., Inc., U.S.P. 2,400,143
[278] Taggart, junr., M. S., Assr. to Standard Oil Development Co., U.S.P. 2,396,900
[279] Rutherford, N. S. and Eisenman, W., Assrs. to Heyden Chem. Co., U.S.P. 2,401,778

ANTIBIOTICS

By F. A. ROBINSON, M.Sc.Tech., LL.B., F.R.I.C.

Allen and Hanburys Limited

THE amount of penicillin produced in this country continues to increase. In 1946, 3,120,000 mega units were produced, in 1947 4,888,000 mega units, in 1948 9,672,000 mega units and in the first ten months of 1949 13,747,000 mega units. These figures are still a long way behind the amount produced in the U.S.A., where the output in the first 10 months of 1949 was about 100,000,000 mega units.

The new issues of the British Pharmacopœia and the British Pharmaceutical Codex contain monographs on penicillin salts, injection solution and oily injection solution of penicillin, penicillin lozenges, penicillin cream and penicillin ointment and eye ointment.

Penicillin fermentation.—A patent has been published[1] describing a continuous method of fermentation with *Penicillium notatum* in which portions of the penicillin-containing liquor are withdrawn at 24- to 48-hourly intervals and replaced with fresh medium. In another patent[2] the use of a medium containing cottonseed meal, lactose and a phenylacetyl derivative is advocated with a composition such that the p_H reaches a value of 6·0 to 8·5 and is maintained at this value for the remainder of the fermentation period. Improved yields are claimed when a medium containing glucose, lactose, an amylaceous product and mineral salts is pre-treated with activated charcoal.[3] The yields obtained by surface culture on a medium containing glucose, lactose, phenylacetic acid, ammonium salts and inorganic salts are said to be increased by the addition of starch and ethylamine to a value comparable with that obtained on a medium containing corn steep liquor.[4]

New mutants of *P. chrysogenum* Q176 have been obtained which are said to produce 50% more penicillin than the parent strains[5]; irradiation with ultra-violet light gives rise to more mutants than does treatment with the nitrogen mustards.

An instructive paper has been published[6] describing the pilot plant used by Eli Lilly & Co. for development work on penicillin, streptomycin and newer antibiotics. The fermentation equipment consists of shake-flasks, 30-l. jar fermenters and 1600-gal. tank fermenters with 85-gal. seed tanks. These enable variables such as speed of aeration and agitation, ingredients of the medium and antifoam agents to be studied in order that the optimal conditions may be determined. The purification section consists of a laboratory which is in effect an organic chemical research laboratory, another devoted almost exclusively to chromatography and a third containing unit process equipment for solvent extraction and hydrogenation.

Isolation and purification.—There are no new developments to report on methods of recovering penicillin from culture fluids, but a method of

drying aqueous solutions of penicillin salts azeotropically by means of light petroleum, chlorobenzene or a mixture of ethylene dichloride and benzene, for instance, has been described,[7] and a patent for spray-drying penicillin salt solutions has been published.[8]

Several new methods of converting crude penicillin into a crystalline salt have been described. Impure amorphous ammonium penicillin for instance can be crystallized by dissolving in a small amount of water, adding a suitable alcohol or ketone and cooling.[9] The purified ammonium salt can be converted into the salt of an alkali metal by adding an alkali carbonate or bicarbonate and distilling at a p_H less than 9.[10] A relatively pure ammonium salt can also be made by treating a solution of penicillin in a suitable organic solvent with the ammonium salt of certain organic acids.[11] Trialkylamines, especially triethylamine,[12] can be used in the same way as other organic bases mentioned in last year's Report for purifying penicillin. Salts of penicillin with a primary base such as *cyclo*hexylamine or a tertiary base such as triethylamine or *N*-ethylpiperidine can be made by adding a salt of the base with a suitable organic acid such as acetic acid to a solution of penicillin in an organic solvent.[13] The salts so formed are converted into alkali metal salts by reacting them with the alkali metal salt of a fatty acid (containing 2 to 8 carbon atoms) in butanol or similar solvent.[14] A similar process using an alkali metal salt of *iso*amylethylacetic acid has been described.[15]

Relatively pure specimens of five species of penicillin were prepared by partition chromatography on columns of silica gel or kieselguhr saturated with a citrate buffer solution.[16]

Assay.—A method of improving the accuracy of the biological assay has been described; large plates containing 64 holes are used instead of petri dishes,[17] enabling 7 instead of 3 test solutions to be assayed. The fiducial limits ($P = 0{\cdot}95$) are $\pm 9{\cdot}6\%$. A method based on the diffusion of penicillin along a capillary tube containing agar seeded with a test organism is said to offer advantages over the conventional procedure for certain types of work.[18] The effect of personal error on routine penicillin assays has been investigated.[19]

Several physical and chemical methods of assay have been described. The most important perhaps is the iodometric method, in which the penicillin is first converted by alkaline hydrolysis into penicilloic acid, which is then estimated iodometrically. The reaction is quantitative provided the conditions used for the hydrolysis and titration are standardized. The results of a collaborative investigation of the method have been published.[20] In another method which is said to give comparable results, but with smaller samples, the penicillin is oxidized by means of potassium ferricyanide, and the excess of the reagent is estimated by titration with ceric sulphate.[21]

Another method of assay depends on the reaction of penicillin with hydroxylamine to form a hydroxamic acid which with iron gives a colour the intensity of which is proportional to the penicillin concentration. It has been applied to the estimation of penicillin in broths and extracts by salting out the ammonium salt into *n*-butanol by means of ammonium sulphate.[22]

The absorption spectra of penicillin in the ultra-violet and infra-red regions have been used for its estimation[23]; the β-lactam ring exhibits a characteristic band at 5·6 μ., which is suitable for assay.

Attempts to find improved methods of estimating benzylpenicillin in a mixture of penicillins have continued. Precipitation with *N*-ethylpiperidine from a selective solvent,[24] the Kapeller–Adler method after removal of other phenylacetyl derivatives that would otherwise interfere,[25] and hydrolysis to liberate the acyl groups characteristic of the different species of penicillin followed by chromatographic separation on a column of Celite[26] have all been used, but Levi and Goodall's method, referred to in last year's Report, probably remains the most satisfactory method of differential assay; it has been modified to enable the benzylpenicillin content of broths to be estimated.[27]

Preparations.—The use of the procaine salt of benzylpenicillin was referred to in last year's Report. Since that time its clinical value, especially in the form of an oil suspension, has been fully established and such suspensions are now universally employed; one injection gives a therapeutic blood level that lasts for a far longer period than does that produced by any other penicillin preparation, especially if the procaine penicillin is in a finely divided state and aluminium stearate is used as suspending agent. Thus when various penicillin preparations were injected into mice infected with *Pneumococcus*, the percentage of survivors after 7 days were[28]: with aqueous sodium penicillin solution, 0; aqueous procaine penicillin suspension, 7; suspension of procaine penicillin in oil, 13; suspension of sodium penicillin in beeswax-oil, large and small particles respectively, 84, 40; suspension of procaine penicillin in oil with aluminium stearate, large and small particles respectively, 66, 100. The injection of 300,000 units of a preparation such as the last-mentioned gave therapeutic blood levels in humans that lasted for 24 hours.[29] Several patents relating to procaine penicillin suspensions have been applied for in this country.

The L-ephedrine salt of penicillin G has been suggested as an alternative to the procaine salt, but appears to be less effective[30]; species of penicillin other than benzylpenicillin (penicillin G) that have given promising results are allylthiomethylpenicillin (penicillin O or AT) and *n*-butylthiomethylpenicillin (penicillin BT).[31]

It has been reported[32] that certain degradation products of benzylpenicillin and *n*-amylpenicillin may enhance the activity of the crystalline salts, providing an explanation of the superior clinical effectiveness of the amorphous salts. Formaldehyde-treated protein penicillin preparations are said[33] to give prolonged blood levels in rabbits and humans; the addition of 'Tweens' prolongs the action still more.

Preparations suitable for oral administration are obtained by mixing a penicillin salt with a neutral or alkaline antacid that does not give off carbon dioxide under acid conditions, e.g. salts of citric acid, tartaric acid or phosphoric acid[34]; or a penicillin salt may be mixed with egg albumen, skimmed milk powder or whey powder.[35] The use of enteric-coated capsules for penicillin has been patented.[36]

Disappointing results have been obtained with esters of penicillin. It was hoped that these on injection would slowly release free penicillin,

thus maintaining a therapeutic blood level over a long period of time. The methyl, ethyl, allyl, benzyl, phenylethyl and related esters of penicillin were prepared by the action of the appropriate diazoalkane on penicillin,[37] but, although more effective than sodium penicillin in protecting mice against *S. haemolyticus*, they were ineffective in higher animals, because in these species hydrolysis did not take place.

Chemistry of penicillin.—The promised monograph with this title was published last year. It is a substantial volume, in which is collected together all the information accumulated during the 2½ years of Anglo-American collaboration on the structure and synthesis of penicillin. It is not a text-book, but a genuine source book of material otherwise available only in some 700 reports circulated among the workers concerned. Each chapter contains a systematic survey of the work done by all the collaborators in a particular field, with full experimental details. In addition to chapters on degradation experiments, on attempts to synthesize penicillin and on the synthesis of intermediates and model substances, there are chapters on the infra-red absorption spectra of penicillin and related substances, on the application of *X*-ray analysis and other physical methods to the elucidation of chemical structure, on biosynthesis and on methods of assay.

Work carried out after the collaboration between research workers in this country and the U.S.A. had ceased has been published in the journals in the ordinary way. Reference was made to some of this subsequent work in last year's Report. Since then numerous other papers and some patents have been published, but as they relate mainly to the preparation of intermediates required for the synthesis of penicillin, they are regarded as falling outside the scope of this review—at all events until the large scale synthesis of penicillin appears to be practicable. It is perhaps worth recording, however, that β-propiolactam (2-azetidinone), the ring compound from which penicillin is derived, has been synthesized by the action of ethyl magnesium bromide on β-alanine[38]; it has no appreciable antibacterial activity on *S. aureus* and is much more stable than penicillin. The synthesis of penicillin by the interaction of D-penicillamine and a 4-alkoxymethylene-5-oxazolone substituted in the 2-position has been patented.[39]

Streptomycin

Streptomycin is now being produced in this country in adequate amounts, but actual figures are not available.

By the Streptomycin Regulations 1948 (S.I. 1948, No. 1735), streptomycin is a substance to which the Penicillin Act 1947 applies, so that it can only be supplied against a prescription or administered by a medical practitioner or under his direction. By the Therapeutic Substances Amendment Regulations 1949 (S.I. 1949, No. 1846), streptomycin was added to the schedule of substances coming within the scope of the Therapeutic Substances Act, 1925. The Regulations define the unit and provide that the minimum potency of streptomycin in the solid state shall be 300 units per mg. and in solution 2000 units per ml. Tests for toxicity, pyrogenicity, and freedom from histamine-like substances are laid down.

Recent clinical reports[40] confirm that streptomycin is the most useful drug so far discovered for the treatment of tuberculosis, but that it has the serious disadvantage of inducing streptomycin-resistance in the organism so that after a time further treatment becomes valueless. Attempts are being made to minimize this defect by simultaneous administration of another antitubercular drug such as *p*-aminosalicylic acid, promizole, sulphonamides or even penicillin.[41] Tests are also being carried out with the streptomycin salt of *p*-aminosalicylic acid.[42]

Another serious disadvantage of streptomycin is that it produces neurotoxic symptoms which may be permanent. Such symptoms are less apparent with dihydrostreptomycin[43] which may for that reason ultimately displace the parent compound in the treatment of tuberculosis.

Streptomycin has given promising results in Gram-negative urinary-tract infections, tularemia, brucellosis, pertussis, non-gonococcal urethritis, actinomycosis, influenzal meningitis and pneumonic plague. In some of these conditions, however, it may prove to be less satisfactory than the more recently discovered antibiotics, chloramphenicol and aureomycin.

Streptomycin fermentation.—Three fermentation patents have been published during the year. One claims the use of a medium containing meals, flours and meal- or flour-infusions of beans, peanuts, cottonseed or linseed as the sole source of nitrogenous and growth-promoting substances.[44] The second patent claims the use of a medium containing soya beans,[45] whereas the third claims a medium containing carbohydrate, mineral nutrients and a non-protein source of nitrogen such as an amino-acid, ammonium salts or nitrates; the addition of citric acid is advantageous.[46] Histidine is said to be essential for both mycelium production and streptomycin production, whereas valine stimulates only the latter and aspartic acid and glutamic acid only the former. With high concentrations of sodium chloride, most of the streptomycin is found in the medium whereas with low concentrations the streptomycin remains in the mycelium.[47] The use of a dimethylsiloxane as an anti-foaming agent in streptomycin fermentations has been patented.[48]

Mutants of *Streptomyces griseus* can be obtained by irradiation with *X*-rays or ultra-violet light; the former gives rise to the larger number of mutants. Unfortunately, mutants that give high yields of streptomycin are generally unstable and quickly revert. Of the mutants obtained, less than 0·1% proved to be both good streptomycin producers and stable.[49] The original strain of *S. griseus*, which does not now produce streptomycin, can be re-activated by *X*-ray treatment.[50]

In the early days of streptomycin manufacture, infection of cultures with actinophage caused considerable trouble, involving on occasion a complete shut-down of the plant. Two types of phage were distinguished, one (Type I) to which resistance was readily acquired by *S. griseus*, and another (Type II) that did not induce the formation of phage-resistant strains. It was eventually found that the addition of sodium citrate or the sodium salts of other polycarboxylic acids to phage-susceptible cultures was effective in preventing the development of both types of phage.[51]

Isolation and purification.—Streptomycin can be recovered from culture fluids on which *S. griseus* has been grown by adsorption on charcoal under neutral or slightly alkaline conditions, followed by elution with

aqueous acid[52]; or it may be adsorbed on a static bed of charcoal, preferably phosphoric acid activated, from an acid solution (p_H 3) and eluted with an aqueous acid, preferably 0·8% sulphuric acid[53]; or it may be adsorbed on a column of synthetic inorganic base exchange alumino-silicate and eluted with sodium hydroxide solution.[54] Elution from charcoal is facilitated if this is pre-treated with a solution containing the sulphuric ester of a saturated alcohol containing between 10 and 18 carbon atoms, e.g. lauryl sulphuric ester.[55] The antibiotic potency of crude or partially purified streptomycin solutions is said to increase if left at p_H 0·5 to 4·5.[56] Histamine can be removed from solutions of streptomycin by adsorption on an inorganic base exchange medium and selectively eluting the streptomycin with dilute salt solution.[57]

Crude streptomycin can be purified by adsorbing from an aqueous solution of p_H 2 to 10 on a surface-active clay and eluting with a solution of the salt of a steam-volatile acid, such as pyridine sulphite or acetate.[58] Crude streptomycin hydrochloride can also be purified by conversion into the sulphate by reacting with the sulphate of an organic base dissolved in water or a lower aliphatic alcohol and then precipitating by means of a suitable solvent.[59] Streptomycin salts and salts of related antibiotics can also be purified by adsorption on a column of a suitable adsorbent followed by selective elution; by precipitation of the picrate; by forming a crystalline salt with an arylazosulphonic acid such as helianthin; or by adding an alkaline-earth halide to form, for example, the double salt of streptomycin hydrochloride and calcium chloride.[60]

Streptomycin and streptomycin B (mannosidostreptomycin) have been separated by counter-current extraction from an aqueous phosphate–borate buffer solution by means of amyl alcohol containing lauric acid.[61] A similar method using amyl alcohol containing stearic acid in a Craig separator is advocated for distinguishing between the two type of streptomycin; more efficient separation occurs than with toluenesulphonic acid in butanol which has previously been used for this purpose.[62]

Streptomycin is converted into dihydrostreptomycin by hydrogenation in the presence of a noble metal catalyst such as platinum.[63] Dihydrostreptomycin sulphate can be crystallized from methyl ethyl ketone or methanol and has a potency of 815 to 830 mg. per g., slightly different values being obtained according to the method of assay.[64] Both streptomycin and dihydrostreptomycin give crystalline salts with naphthalene-β-sulphonic acid.[65]

Assay.—A capillary tube method for the microbiological assay of streptomycin has been described.[66] Further details have been published of the colorimetric method of estimating mannosidostreptomycin by means of a 0·2% solution of anthrone in 98% sulphuric acid.[67] A new modification of the maltol method of assay has been proposed. An alkaline solution of streptomycin is heated in boiling water for 3 minutes, forming maltol, and sulphuric acid and ammonium sulphate are then added and the solution is distilled to remove the maltol. Ferric chloride solution is added to the distillate and the colour is evaluated at 550 mμ.[68]

Chemistry of streptomycin and related compounds.—Mannosidostreptomycin has been shown to be a D-mannosido-*N*-methyl-α-L-glucosaminido-L-streptoside of streptidine.[69]

Preparations.—Up to the present, no attempt appears to have been made to use derivatives of streptomycin to improve its clinical efficacy, and streptomycin and dihydrostreptomycin are generally administered in the form of their hydrochlorides or sulphates and, with the former, its calcium chloride complex. The only important developments are those relating to the simultaneous administration of other anti-tubercular substances already referred to. W. A. Winsten,[70] however, has shown that streptomycin-resistant strains of *S. aureus* are inhibited by *N*-*n*-propyl-, *N*-*n*-butyl- and *N*-*n*-decyl-streptomycylamines, an observation that may have important consequences in due course.

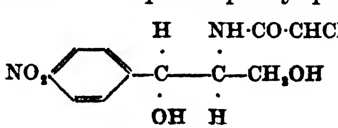
Chloramphenicol and aureomycin

Penicillin still retains its position as the most important antibiotic, with streptomycin occupying second place. The view expressed in last year's Report that chloromycetin and aureomycin would become important has been confirmed and both are being used clinically. Chloromycetin, now given the non-proprietary name of chloramphenicol, has given good results in certain virus and rickettsial infections and shows promise also in the treatment of typhoid, cholera and syphilis; but it appears to have a rather restricted field of application. Aureomycin, on the other hand, has a much wider antibacterial spectrum and is active against several viruses and rickettsiae and Gram-positive and Gram-negative bacteria. It is effective against penicillin- and streptomycin-resistant strains of these bacteria, and may ultimately displace the two older antibiotics in the treatment of certain infections, as it appears to induce drug resistance less readily. Aureomycin has given promising results in the treatment of brucellosis, syphilis, amoebiasis, pertussis, primary atypical pneumonia, staphylococcal meningitis and staphylococcal bacteremia.

The present status of the four most important antibiotics is summarized in the following table, which shows the antibiotics that are effective against the various groups of micro-organisms; where two or more antibiotics are effective, these are given in decreasing order of effectiveness.

Micro-organisms	Antibiotics
Lymphogranuloma and psittacosis viruses	Aureomycin, penicillin, chloramphenicol
Rickettsiae	Chloramphenicol, aureomycin
Anaerobes	Penicillin
Gram-positive bacteria	Penicillin, aureomycin, streptomycin, chloramphenicol
Spirochaetes	Penicillin, aureomycin
Brucella	Aureomycin, chloramphenicol
Gram-negative bacteria	Chloramphenicol, aureomycin, streptomycin
Plague and dysentery bacteria	Streptomycin
Acid-fast bacteria	Streptomycin

Chemistry of chloramphenicol.—Chloramphenicol has been shown to be D(-)-threo-2-dichloroacetamido-1-*p*-nitrophenyl-propane-1 : 3-diol[71] and is



the first example of an aromatic nitro-compound in a substance of natural origin. This structure has been confirmed by synthesis[72,73]; the methods used are discussed in the chapter on Fine Chemicals and Medicinal Substances

Aureomycin.—No information has yet been published on the methods used to produce aureomycin, but its properties have been described.[74] It is a golden-yellow crystalline compound, melting at 168–169° c. It is a weak optically-active base, containing nitrogen and non-ionic chlorine. The analytical values obtained correspond with an empirical formula of $C_{24}H_{27}N_2O_7Cl$, but nothing has yet been published concerning its structural formula. Aureomycin is stable in the dry state, but rapidly loses activity in aqueous solution at 37° c.

Aureomycin can be assayed microbiologically either by the serial dilution method using a haemolytic streptococcus[75] or *B. cereus* var. *mycoides*,[76] or by titration with *S. aureus* using the change in colour of phenol red resulting from the fermentation of glucose by still-viable organisms as the end-point.[77] A chemical method of assay has been described, based on the development of a blue fluorescence in a buffer solution of p_H 7·5 or on the formation of a yellow colour on heating with hydrochloric acid.[78]

Other *Streptomyces* antibiotics

A *Streptomyces* antibiotic that shows considerable promise is neomycin. This is produced by an organism closely related to *S. fradiae*, which can be grown either by surface or submerged culture on a medium containing carbohydrate, a source of nitrogen and salts.[79] Neomycin is recovered from the culture fluid by adsorption on charcoal and elution with acid. It is inhibitory to many Gram-positive and Gram-negative bacteria, and has a different antibacterial spectrum from those of streptomycin and streptothricin. Bacteria do not readily become resistant to neomycin and its toxicity is low. It is bactericidal and is more effective than streptomycin against *S. aureus* and *E. typhosa*; it is also effective against *M. tuberculosis*.

Actually, neomycin appears to be a mixture of at least three antibiotics; these have been separated by a combination of adsorption on Decalso, followed by elution with ammonium chloride solution, chromatographic adsorption on charcoal and precipitation with picric acid.[80]

Another interesting new *Streptomyces* antibiotic is actinomycin, produced by *A. antibioticus* and another species not yet identified. The mould is grown on a medium containing soya bean, brown sugar, corn steep liquor and potassium phosphate, and the antibiotic is recovered from the culture fluid by extraction with butanol. The extract is evaporated and the residue crystallized from warm ethanol.[81] It is a red substance with the empirical formula $C_{41}H_{54}O_{12}N_8$ and yields threonine L-proline, D-valine and *N*-methylvaline on hydrolysis[82]; it appears to be a peptide in combination with a quinone.

Antimycin A is another new antibiotic and is produced by an unidentified *Streptomyces* species. It is an optically active nitrogeneous phenol with the formula $C_{28}H_{40}O_9N_2$, and has a remarkably high fungicidal activity.[83]

S. griseus produces several other antibiotics in addition to streptomycin. Two new ones hve been described recently. One has been designated 'Antibiotic 3510' and the other streptocin. The former is effective against streptomycin-resistant bacteria and protects chick embryos against *Salmonella pullorum*,[84] whereas streptocin possesses strong trichomonadicidal properties and inhibits the growth of Gram-positive bacteria.[85] It is extracted from the culture fluid by means of ether, but is different from actidione, another ether-soluble antibiotic produced by *S. griseus*. *S. lavendulae* also produces several antibiotics in addition to streptothricin. One of these, designated 'streptothricin VI,' is very similar to streptothricin in chemical and antibacterial properties, but is a little less toxic. It is isolated by adsorption on Decalso and elution with ammonium chloride solution or by adsorption on charcoal and elution with methanolic formic acid.[86] Streptothricin, like streptomycin, forms a calcium chloride double salt.[87]

Bacterial antibiotics

In spite of the fact that no bacterial antibiotic has so far proved to be clinically effective, this group of substances has been intensively studied in recent months. Many of them are peptides and the application of paper partition chromatography has enabled tremendous advances to be made towards elucidating their structures.

Gramicidins and tyrocidins.—Gramicidin and tyrocidin are the names originally given to a neutral substance and a basic substance produced by *B. brevis*. Gramicidin was separated into four components by partition between buffer solution and solvent,[88] and tyrocidin into several components by chromatographic adsorption on charcoal.[89] Partial hydrolysis of gramicidin yielded a mixture of peptides including three identified as D-leucylglycine, L-alanyl-D-valine and L-alanyl-D-leucine.[90] From diffusion experiments the molecular weight of gramicidin was found to be between 2800 and 5000 and that of tyrocidin between 1900 and 5100; the molecular weight of gramicidin S, which contains five amino-acids, indicates that it is a *cyclo*decapeptide.[91] Methylolgramicidin has only 0·1 to 1·2% of the toxicity of gramicidin, whilst other derivatives possess intermediate toxicities; none of them, however, could be administered intravenously.[92]

Subtilin and bacitracin.—Subtilin has been produced by submerged culture of *B. subtilis* in 200-l. tanks.[93] Its antibacterial activity is increased by esterification with methanol, but decreased by esterificaton with ethanol.[94] Although it has a moderate effect *in vitro* on *M. tuberculosis* it is ineffective *in vivo*.[95] Bacitracin, also produced by *B. subtilis*, yielded a single pure substance on counter-current distribution, and gave a mixture of amino acids and peptides on hydrolysis.[96] Bacitracin was very effective by topical application in pyogenic dermatoses,[97] and gave a favourable response in a high proportion of cases of surgical infections that had failed to respond to sulphonamides and other antibiotics.[98]

Of 165 strains of aerobic spore-forming bacilli tested, all those belonging to the *B. subtilis* group yielded antibiotics.[99] Three new antibiotics isolated from cultures of *B. subtilis* have been named bacilipin A, bacilipin

B and bacilysin; the first two are aliphatic nitrogen-containing acids and the third a peptide.[100]

Polymyxins.—To emphasize its relationship to other members of the polymyxin group, aerosporin has been re-named polymyxin A, whilst the substance previously known as polymyxin is now known[101] as polymyxin D. Polymyxin A is isolated from culture fluids of *B. aerosporus* (*B. polymyxa*) by adsorption on charcoal, preferably after heating the fluid under acid conditions, and then eluting the adsorbate with a solvent such as aqueous acetone acidified with sulphuric acid. The crude preparation may be purified, *inter alia*, by re-dissolving in water and filtering, converting to the hydrochloride, dissolving in methanol and re-precipitating with ether, precipitating with picric acid or fractionally precipitating with methyl orange.[102] The polymyxins can also be purified by converting to their naphthalene-β-sulphonic acid salts; polymyxin B was obtained as a crystalline hydrochloride and polymyxin E as a crystalline neutral sulphate. All the polymyxins yield the same optically active fatty acid on hydrolysis; this has now been identified as *dextro*-6-methyloctan-1-oic acid.[103] Polymyxin B has also been purified by conversion to the Polar Yellow salt.[104] Methods used for the production and isolation of the various polymyxins were discussed at a symposium held by the New York Academy of Sciences.[105] Polymyxins A, B, D and E strongly inhibit the growth of Gram-negative organisms, and polymyxins A, B and E have been tried out in urinary tract infections, but with limited success; they caused neurotoxic symptoms which however disappeared when treatment ceased.[106]

A new member of the polymyxin family is circulin. Actually two different substances were originally described under this name. One of these, discovered by C. McLeod,[107] has been re-named polypeptin; the other, discovered by F. J. Murray *et al.*,[108] retains the name circulin. The latter has an antibacterial spectrum similar to that of the polymyxins and inhibits Gram-negative organisms more readily than Gram-positive organisms. It is less toxic than polymyxin A but more toxic than polymyxin D, and protects mice against *E. typhosa* and *Kl. pneumoniae.*[108,109] It is produced by *B. circulans*, and can be isolated from culture fluids by adsorption on charcoal and elution with acid butanol and purified by chromatography on charcoal. It is basic polypeptide with the formula $(C_{39}H_{74}C_9N_{12})n$; on hydrolysis it yields the same amino-acids as polymyxins A and E, namely leucine, threonine and $\alpha\gamma$-diamino-butyric acid, together with the optically-active fatty acid.[110]

Miscellaneous bacterial antibiotics.—New antibiotics described recently include an antibiotic from *B. mesentericus* that inhibits *C. diphtheriæ*[111]; laterosporins A and B which were isolated from *B. laterosporus* culture fluids by adsorption on charcoal and elution with acid butanol, purified by conversion to the picrate and shown to be peptides[112]; alvein, produced by deep culture of *B. alvei* on a corn steep liquor medium, isolated and purified by similar methods and also shown to be a peptide[113]; biocerin, produced by *B. cereus* and mainly active on Gram-negative organisms[114]; micrococcin produced by a species of *Micrococcus* isolated from sewage and inhibitory to Gram-positive bacteria, *Mycobacteria* and actinomycetes[115]; and a protein antibiotic produced by *S. aureus* with a wide antibacterial spectrum but rather low potency.[116]

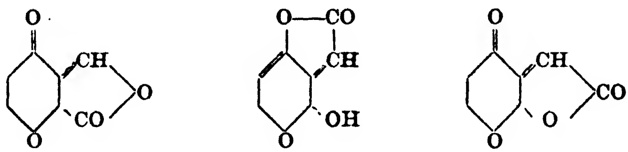
A little further information has been published about licheniformin. This is produced by *B. licheniformis*, which is grown in shallow layers under neutral or alkaline conditions. The addition to the medium of amino-acids and yeast extract speeds up production but does not increase the yield.[117]

One of the more promising bacterial antibiotics is nisin. This is bactericidal *in vitro* and *in vivo* and its toxicity depends on the route of administration. It synergizes with streptomycin and licheniformin and, given subcutaneously, it limits the spread of experimental tuberculosis.[118] It is produced by *Streptococcus lactis* (Lancefield Group N) on a medium containing glucose, yeast extract and Lemco. The culture fluid is acidified to p_H 1·9 and, after standing for a day or two, it is neutralized to p_H 5, emulsified with chloroform and the supernatant solution discarded. The emulsion is distilled and the aqueous residue filtered, boiled to destroy enzymes, concentrated 5-fold, acidified and treated with alcohol and ether to remove impurities and then treated with more of the solvent mixture to precipitate the nisin. This appears to be a small protein or a large polypeptide[119]; it is at present undergoing trials in bovine mastitis.

Mould antibiotics

Of the many mould antibiotics that have been described, only penicillin has found a place in therapeutics. In spite of this, mould antibiotics continue to offer an attractive field for chemical investigation, and new strains of mould are still being examined for antibiotic production.

The structure of patulin is the subject of controversy between two different groups of workers. Originally given formula (I) by H. Raistrick, formula (II) has recently been advanced by R. B. Woodward and G. Singh[120] and formula (III) by B. G. Engel *et al.*[121]

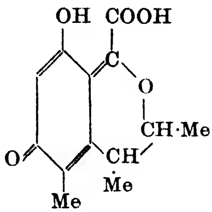


(I) (II) (III)

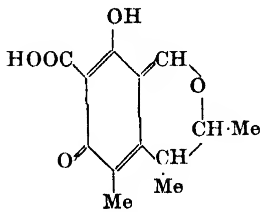
The evidence for the new structures is outside the scope of this review, but R. B. Woodward and G. Singh claim to have synthesized desoxypatulin with a structure analogous to (II), whereas H. J. Dauben and F. L. Weisenborn[122] claim that the infra-red spectrum of patulin has a band characteristic of the O–H bond. B. G. Engel, however, asserts that patulin cannot possess a free hydroxyl group, and a decision between formulæ (II) and (III) will have to await further evidence.

The structure assigned to citrinin by N. J. Cartwright *et al.*,[123] for which the complete evidence has now been published, has been challenged by E. Schwenk *et al.*[124] and A. H. Frye *et al.*[125] who propose formula (IV), although a substance with the structure represented by formula (V) was synthesized by the British workers and found to be identical with citrinin. Dihydrocitrinin has been synthesized.[126]

Of 37 species of *Aspergilli* tested, 20 produced antibiotics.[127] Two species produced penicillic acid, two others kojic acid and two others, *A. caespitosus* and *A. quadrilineatus*, penicillin-like substances. Penicillin-like substances were also produced by several species of *Penicillium*—*P. meleagrinum*, *P. euglaucum*, *P. divaricatum*, and *P. roseo-citreum*.[128]



(IV)



(V)

Another species produced penicillic acid, two others mycophenolic acid and two others patulin. *P. herquei* produced a new antibiotic which has been named herquein,[128] whilst *A. candidus* produced a new antibiotic termed candidulin, which was effective *in vitro* against acid-fast organisms, but was inactive in experimental mouse tuberculosis.[129]

References

1 Moyer, A. J., B.P. 624,411
2 Merck & Co., Inc., B.P. 631,126
3 Carbonisation et Charbons Actifs, B.P. 624,108
4 Calam, C. T. and Hockenhull, D. J. D., *J. gen. Microbiol.*, 1949, **3**, 19
5 Reese, E. *et al.*, *J. Bact.*, 1949, **57**, 15
6 Fortune, W. B. *et al.*, *Ind. Eng. Chem.*, 1950, **42**, 191
7 Merck & Co., Inc., B.P. 622,305
8 Heyden Chemical Corpn., B.P. 625,924
9 Commercial Solvents Corpn., B.P. 628,251
10 Idem, B.P. 630,254
11 Glaxo Laboratories, Ltd., B.P. 624,759
12 Heyden Chemical Corpn., B.P. 629,662
13 Glaxo Laboratories, Ltd., B.P. 626,027, 630,462
14 Idem, B.P. 622,988
15 Eli Lilly & Co., B.P. 626,417
16 Levi, A. A., *Biochem. J.*, 1948, **43**, 257; Boon, W. R. *et al.*, ibid., 262; Dobson, F. and Stroud, S. W., ibid., 1949, **45**, *Proc.*, i
17 Browlee, K. A. *et al.*, *J. gen. Microbiol.*, 1949, **3**, 347
18 Davis, W. W. *et al.*, *Science*, 1949, **109**, 545
19 Young, P. A., *Brit. J. Pharmacol.*, 1949, **4**, 366
20 Analyst Sub-Committee to the Ministry of Health Conference, *Analyst*, 1949, **74**, 650
21 Hiscox, D. J., *Analyt. Chem.*, 1949, **21**, 658
22 Henstock, H. I., *Nature*, 1949, **164**, 139
23 Levy, G. B. *et al.*, *Analyt. Chem.*, 1948, **20**, 1159; Coy, N. H. *et al.*, ibid., 1949, **21**, 669
24 Levy, G. B. *et al.*, ibid., 1949, **21**, 664
25 Boxer, G. E. and Everett, P. M., ibid., 670
26 Higuchi, K. and Peterson, W. H., ibid., 659
27 Karnovsky, M. L. and Johnson, M. J., ibid., 1125
28 Miller, A. K. *et al.*, *Proc. Soc. exp. Biol., N.Y.*, 1949, **70**, 313
29 Young, M. Y. *et al.*, *Lancet*, 1949, **1**, 863
30 Grunberg, E. *et al.*, *J. Pharmacol.*, 1949, **95**, 336

[31] Rose, C. L. *et al.*, *J. Lab. clin. Med.*, 1949, **34**, 426; Bliss, E. A. and Todd, H. P., *J. Bact.*, 1949, **58**, 61
[32] Hobby, G. L. *et al.*, *J. Bact.*, 1949, **57**, 247
[33] Loewe, L. *et al.*, *J. Lab. clin. Med.*, 1949, **34**, 67
[34] Wyeth Inc., B.P. 617,873
[35] Merck & Co., Inc., B.P. 629,281
[36] American Cyanamid Co., B.P. 613,524
[37] Kirchner, F. K. *et al.*, *J. org. Chem.*, 1949, **14**, 388; Merck & Co., B.P. 630,264
[38] Holley, R. W. and Holley, A. D., *J. Amer. chem. Soc.*, 1949, **71**, 2129
[39] Merck & Co., B.P. 630,284
[40] *See*, e.g. *Lancet*, 1949, (i), 273; *J. Amer. med. Ass.*, 1949, **139**, 634; *Proc. R. Soc. Med.*, 1949, **62**, 155
[41] Spink, W. W. *et al.*, *J. Amer. med. Ass.*, 1949, **139**, 352; Pulaski, E. J. and Baker, H. J., *J. Lab. clin. Med.*, 1949, **34**, 186; Moeschlin, S. *et al.*, *Helv. med. Acta*, 1948, **15**, 535; Lincoln, E. M. and Kirmse, T. W., *Lancet*, 1949, (i), 767
[42] Adcock, J. D. *et al.*, *Proc. Soc. exp. Biol., N.Y.*, 1949, **72**, 451
[43] Edison, A. O. *et al.*, *Amer. Rev. Tuberc.*, 1948, **58**, 487; Hobson, L. B. *et al.*, ibid., 501; Hinshaw, H. C. *et al.*, ibid., 525
[44] Squibb, E. R. & Co., B.P. 613,469
[45] Ayerst, McKenna & Harrison, B.P. 616,331
[46] Boots Pure Drug Co., Ltd., B.P. 616,102
[47] Eiser, H. M. and McFarlane, W. C., *Canad. J. Res.*, 1948, **26C**, 164
[48] Distillers Company, Ltd., B.P. 631,507
[49] Savage, G. M., *J Bact.*, 1949, **57**, 429
[50] Waksman, S. A. and Harris, D. A., *Proc. Soc. exp. Biol., N.Y.*, 1949, **71**, 232
[51] Koerber, W. L. *et al.*, Abstracts of Communications to the 1st International Congress of Biochemistry, 1949, 560
[52] Wellcome Foundation, Ltd., B.P. 611,984
[53] The Distillers Company, Ltd., B.P. 619,566
[54] Idem, B.P. 616,955
[55] Idem, B.P. 622,982
[56] Idem, B.P. 616,438
[57] Idem, B.P. 625,146
[58] Abbott Laboratories, B.P. 629,479
[59] Boots Pure Drug Co., Ltd., B.P. 622,564
[60] Merck & Co., Inc., B.P. 625,820, 625,821, 626,469, 620,415
[61] O'Keeffe, A. E. *et al.*, *J. Amer. chem. Soc.*, 1949, **71**, 2452
[62] Plant, G. W. E. and McCormack, R. B., ibid., 2264
[63] Parke, Davis & Co., B.P. 630,383
[64] Solomons, I. A. and Regna, P. P., *Science*, 1949, **109**, 515; Wolf, F. J. *et al.*, ibid., 515
[65] Regna, P. P. and Carboni, R. A., *J. Amer. chem. Soc.*, 1949, **71**, 2939
[66] Mitchison, D. A. and Spicer, C. C., *J. gen. Microbiol.*, 1949, **3**, 184
[67] Emery, W. B. and Walker, A. D., *Analyst*, 1949, **74**, 455; Perlman, D., *J. biol. Chem.*, 1949, **179**, 1147; Kowald, J. A. and McCormack, R. B., *Analyt. Chem.*, 1949, **21**, 1383
[68] Eisenman, W. and Bricker, C. E., *Analyt. Chem.*, 1949, **21**, 1507
[69] Stavely, H. E. and Fried, J., *J. Amer. chem. Soc.*, 1949, **71**, 135
[70] Winsten, W. A., *J. clin. Invest.*, 1949, **28**, 850
[71] Rebstock, M. C. *et al.*, *J. Amer. chem. Soc.*, 1949, **71**, 2459
[72] Controulis, J. *et al.*, ibid., 2463
[73] Long, L. M. and Troutman, H. D., ibid., 2469, 2473
[74] Broschard, R. W. *et al.*, *Science*, 1949, **109**, 199
[75] Brainerd, H. D. *et al.*, *Proc. Soc. exp. Biol., N.Y.*, 1949, **70**, 318
[76] Schneierson, S. S. and Toharsky, B., *J. Bact.*, 1949, **57**, 483
[77] Valentine, F. C. O. and Johns, R. G. S., *Lancet*, 1949, (ii), 1033
[78] Levine, J. *et al.*, *J. Amer. pharm. Ass., Sci. Ed.*, 1949, **38**, 473
[79] Waksman, S. A. and Lechevalier, H. A., *Science*, 1949, **109**, 305; Waksman, S. A. *et al.*, *J. Bact.*, 1949, **58**, 229; *J. clin. Invest.*, 1949, **28**, 934
[80] Swart, E. A. *et al.*, *Arch. Biochem.*, 1949, **24**, 92
[81] Lehr, H. and Berger, J., ibid., 1949, **23**, 503
[82] Dalgleish, C. E. and Todd, A. R., *Nature*, 1949, **164**, 830

[83] Dunslee, B. R. *et al.*, *J. Amer. chem. Soc.*, 1949, **71**, 2436
[84] Garson, W. and Waksman, S. A., *Proc. nat. Acad. Sci., Wash.*, 1948, **34**, 232
[85] Waksman, S. A. *et al.*, *Proc. Soc. exp. Biol., N.Y.*, 1949, **70**, 308
[86] Hutchison, D. *et al.*, *Arch. Biochem.*, 1949, **22**, 16
[87] Merck & Co., Inc., B.P. 620,413
[88] Gregory, J. D. and Craig, L. C., *J. biol. Chem.*, 1948, **172**, 839
[89] Synge, R. L. M. and Tiselius, A., *Acta chem. scand.*, 1947, **1**, 749; 1949, **3**, 231
[90] Synge, R. L. M., *Biochem. J.*, 1949, **44**, 542
[91] Pedersen, K. O. and Synge, R. L. M., *Acta chem. scand.*, 1948, **2**, 408
[92] Schales, O. and Mann, G. E., *Arch. Biochem.*, 1948, **18**, 217
[93] Garibaldi, J. A. and Feeney, R. E., *Ind. Eng. Chem.*, 1949, **41**, 432
[94] Carson, J. F. *et al.*, *J. Amer. chem. Soc.*, 1949, **71**, 2318
[95] Steenken, W. and Wolinsky, E., *J. Bact.*, 1949, **57**, 305
[96] Craig, L. C., *J. clin. Invest.*, 1949, **28**, 1014
[97] Derzavis, J. L. *et al.*, *J. Amer. med. Ass.*, 1949, **141**, 191
[98] Meleney, F. L. *et al.*, *Ann. Surg.*, 1948, **128**, 714
[99] Gilliver, K., *Brit. J. exp. Path.*, 1949, **30**, 214
[100] Newton, G. G. F., ibid., 1949, **30**, 306
[101] Stansly, P. G. and Brownlee, G., *Nature*, 1949, **163**, 611
[102] Wellcome Foundation, Ltd., B.P. 619,572, 623,255
[103] Wilkinson, S., *Nature*, 1949, **164**, 622
[104] Regna, P. P. *et al.*, *J. clin. Invest.*, 1949, **28**, 1022
[105] Porter, J. N. *et al.*, *Ann. N.Y. Acad. Sci.*, 1949, **54**, 857; Benedict, R. G. and Stodola, F. H., ibid., 866
[106] Bliss, E. A. *et al.*, ibid., 944; Brownlee, G. *et al.*, ibid., 952; Pulaski, E. J. *et al.*, *J. clin. Invest.*, 1949, **28**, 1028; Jawitz, E. and Coleman, V. R., *J. Lab. clin. Med.*, 1949, **34**, 751
[107] McLeod, C., *J. Bact.*, 1948, **56**, 749
[108] Murray, F. J. *et al.*, ibid., 1949, **57**, 305
[109] Bliss, E. A. and Todd, H. P., ibid., 1949, **58**, 61
[110] Peterson, D. H. and Reineke, L. M., *J. biol. Chem.*, 1949, **181**, 95
[111] Miller, J. and Rowley, D., *Brit. J. exp. Path.*, 1948, **29**, 452
[112] Barnes, E. M., ibid., 1949, **30**, 100
[113] Gilliver, K. *et al.*, ibid., 209
[114] Johnson, C. W. *et al.*, *J. Bact.*, 1949, **57**, 163
[115] Su, T. L., *Brit., J. exp. Path.*, 1948, **29**, 473
[116] Gardner, J. F., ibid., 1949, **30**, 130
[117] Belton, F. C. *et al.*, *J. gen. Microbiol.*, 1949, **3**, 400
[118] Hirsch, A. and Mattick, A. T. R., *Lancet*, 1949, (ii), 190
[119] Berridge, N. J., *Biochem. J.*, 1949, **45**, 486
[120] Woodward, R. B. and Singh, G., *J. Amer. chem. Soc.*, 1949, **71**, 758
[121] Engel, B. G. *et al.*, *Helv. chim. Acta*, 1949, **32**, 1166, 1752
[122] Dauben, H. J. and Weisenborn, F. L., *J. Amer. chem. Soc.*, 1949, **71**, 3853
[123] Cartwright, N. J. *et al.*, *J. chem. Soc.*, **1949**, 1563
[124] Schwenk, E. *et al.*, *Arch. Biochem.*, 1949, **20**, 220
[125] Frye, A. H. *et al.*, *J. org. Chem.*, 1949, **14**, 397
[126] Warren, H. H. *et al.*, *J. Amer. chem. Soc.*, 1949, **71**, 3422
[127] Gill-Carey, D., *Brit. J. exp. Path.*, 1949, **30**, 114, 119
[128] Burton, H. S., ibid., 151
[129] Stansly, P. G. and Ananenko, N. H., *Arch. Biochem.*, 1949, **23**, 256

CHEMICAL ENGINEERING, PLANT AND MACHINERY

Chemical Engineering Group

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CHEMICAL engineering literature during the past year is characterized by the large number of papers on the solids fluidization technique. It is clear from the interest shown that this mode of operation is gaining favour in a wide variety of processes, although details of particular applications are not yet published. At a symposium at the Massachusetts Institute of Technology on December 28 and 29, 1948, no less than 21 papers were presented, and many others have appeared in addition.

Industrial and Engineering Chemistry continues to publish Annual Reviews of unit processes in Chemical Engineering but, presumably owing to shortage of space, they tend to be abbreviated and each year certain of the reviewers describe papers of many years' standing; this detracts somewhat from their value as indicators of the rate of progress in the subject.

The volume of literature on gas turbines is decreasing as it becomes apparent that its·most valuable qualities are realized in its application to jet propulsion, where its very high shaft-speed is not a disadvantage and the load is relatively constant. There is no doubt that this engine will take its place in the field of stationary power units, but the design will require radical modification for these specific conditions.

The earlier enthusiasm over the many possible applications of the 'heat pump' has given way to more deeply considered uses for the machine, and its value where large quantities of low-potential heat are involved is being recognized and is reflected in more practical articles on this device.

Fluid flow

The intense interest in fluidized catalysis has resulted in some decrease in work on the flow of fluids in geometrical systems. T. von Karman[1] reviews the development of fluid flow relationships based on Reynolds' experiments, and C. E. Lapple[2] discusses the present equations for flow in pipes and fittings across tube banks and through beds of granular solids. R. Comolet[3] refers again to the fact that in small, perfectly smooth conduits viscous flow may occur at high Reynolds numbers. In 1–4 mm.-tubes 100–500-diam. long laminar flow is possible at Re = 75,000 provided there are no pressure fluctuations.

In 'plastic flow' in pipes the core may flow rod-wise with an annular layer between the main body of fluid and the wall in either viscous or turbulent flow. A modified Reynolds number based on the radius of this zone determines the type of flow. E. L. McMillen[4] outlines the conditions for this type of flow and shows that viscous shearing in the annular zone takes place at Reynolds numbers higher than the critical

value for normal fluids. Methods of predicting core-flow and calculating the pressure drop are indicated.

R. W. Lockhart and R. C. Martinelli,[5] from experiments on two-phase flow in pipes of 0·0586 to 1·017 in. diam., have established correlations for pressure drop and flow rate. The authors reject the normal dimensional analysis approach on the grounds that an almost infinite number of dimensionless groups could be formulated, involving only ratios of similar properties of the components. Instead they use the facts that the pressure drop must be the same for the gas and liquid, and the sum of the volumes of gas and liquid must equal the volume of the system. On this basis a relationship is deduced involving a parameter X equal to the square root of the ratio of pressure drops for liquid and gas flowing alone in the pipe. Although four types of flow are recognized, depending on whether one or both of the components is in streamline or turbulent motion, only an approximate estimate can be made of the conditions giving rise to each type. The authors stress the fact that this is not an absolute solution, but it appears to be a practical basis for calculation. The difficulties of establishing a simple relationship are emphasized by O. P. Bergelin,[6] who has examined the flow of gas and liquid mixtures in a horizontal glass tube. He points out that the addition of only a small quantity of one constituent to the other may cause an increase in the pressure drop of from two to fifty times. He observed that in two-phase flow bubbling, stratification, wave motion, slugging and annular flow exist at varying velocities and concentrations.

Progress in pumping is mainly in the field of rotary pumps. P. F. Martinuzzi[7] draws attention to the great improvement in axial flow compressors brought about by study of these pumps for gas turbine use and he predicts their wider application in chemical work. Adiabatic efficiencies of 85% are common and some large units operate at 88%, while newer laboratory models show efficiencies of over 90%. Compression ratios up to 11 : 1 are practicable but the machines are only suitable for volumes in excess of 6000 cu.ft./min. and their pressure—volume characteristics are very critical. Modern centrifugal compressors with a compression ratio of 4 : 1 and 80% efficiency have been built and they are capable of operating at lower throughputs with more satisfactory pressure–volume characteristics. The axial flow compressor should find application in tonnage oxygen production. F. Flader[8] claims lower weight and general space requirements for axial-flow machines and their popularity is reflected in patents[9,10] on design of impellor blades to improve axial thrust at the expense of centrifugal effect. I. Taylor,[11] in a short article on centrifugal pumps, illustrates two design-modifications which should have extensive application. In one, both inlet and outlet pipes are mounted on the volute casing and the end-plate can be removed to expose the rotor without disconnecting the pipes. An alternative is a pump in which the motor backplate and drive can be removed leaving the pipes and volute connected.

In high-vacuum practice there are comparatively few fundamental advances. The addresses by C. R. Burch and M. L. E. Oliphant at the British–American High Vacuum Convention last year are now published.[12,13] M. Richelson[14] discusses the conditions which must be

satisfied by materials for high-velocity jet pumps. Glass and porcelain are suggested as most suitable for thermal, shock-, corrosion- and abrasion-resistance.

Fluidization symposium

A large number of papers on fluidization has appeared during the year. At a symposium sponsored by the American Chemical Society more than 20 papers were presented, which are recorded in *Industrial and Engineering Chemistry*.[15] The editors of the journal are to be congratulated in recognizing the difficulty of non-standard nomenclature and have collaborated with the writers in rationalizing their definitions and terms. These are tabulated in a paper at the end of the symposium. A clear discrimination is made between a 'moving bed,' which is described as 'particles substantially fixed with reference to each other but moving bodily with respect to the retaining walls,' and a 'fluidized bed,' which is essentially the reverse. A parallel is drawn between a quiescent fluidized bed and a body of liquid at rest, and between turbulent fluidization and a boiling liquid. In fluidization the zones corresponding to vapour and liquid phases in boiling liquid are described as the 'disperse' and 'dense' phases.

Most of the papers are concerned with the physical behaviour of fluidized masses. W. K. Lewis, E. R. Gilliland and W. C. Bauer[16] confine their investigation to fluidization of glass spheres. They find that in deep quiescent beds pressure drop and length are only linearly related, with particles of small diameter. The authors consider the the relationship of velocity of fluidizing medium, fractional voidage and a modified friction factor of the type used in hindered settling. From experiments with different sizes of spheres, and using air and water for fluidization, it is found that the product of the friction factor and a power of fractional voids yields a straight line when plotted against Re for the particles. At low fluid rates, fluidizing velocity is independent of the fluid density and inversely proportional to the viscosity. This lack of dependence on density accounts for the fact observed by other experimenters that essentially the same linear velocity is required for fluidization at atmospheric and reduced pressures. The fraction voidage can be simply related to velocity taking as basic states for both, the quiescent bed. The authors remark on the fact that correlation is most easily effected under conditions where 'slugging' is prevalent. R. D. Morse[17] considers that the most valuable propertes of a fluidized mass are secured only under non-bubbling and particularly non-slugging condititions. This author has re-evaluated the well-known results of Leva and of Wilhelm and Kwauk in a form similar to that proposed by Carman and by Kozeny for fixed beds. Carman and Kozeny independently suggested the relationship of a friction factor involving the voidage fraction with a similarly modified Reynolds number. Leva's results deviate from the Carman–Kozeny line only in slope and this might be accounted for by agglomerate fluidization of the smallest particles studied. Wilhelm and Kwauk's results apply to larger particles in the turbulent velocity range and these cannot be reconciled to the Kozeny line. The author suggest that this may be explained by regarding the bed as consisting of local

rising currents of expanded solid and descending currents of concentrated solid, which leads to higher energy absorption than in regular fluidization. Another explanation of the deviation of results may be the incorrect evaluation of shape factor or equivalent spherical resistance. The difficulty of evaluating shape factor is emphasized by M. Leva, M. Weintraub, M. Grummer and M. Pollchick.[18] They point out that in estimating the voidage fraction and shape factor for anthracite coal, the most effective method is simple comparison with similarly shaped particles of known characteristics.

J. Happle[19] considers flow relations in a bed of solid moving *en masse* through a reactor but independently of the gas velocity. A relationship on the basis of the Kozeny equation appears to apply and deviations are attributed to the difficulty of evaluating the voidage and shape factor.

G. L. Matheson, W. A. Herbst and P. H. Holt[20] have examined the density and viscosity variations in a fluidized bed. It is interesting to note that although a simple law relates these variables to particle size, particle density and gas velocity, the exception is for spheres which exhibit an abnormally high bed-density. This may only show that the choice of 'mean diameter' for irregular particles is not effective but an abnormal pressure-drop-length ratio for spheres has been noted by Lewis *et al.* (*loc. cit.*). As would be expected the viscosity of the bed decreases rapidly with increase in fluid velocity till a quiescent mass is formed, after which there is less marked fall in viscosity. The rate of change of viscosity is highest with small particles so that addition of small quantities of fines greatly increases the viscosity of a catalyst bed. A parallel with pure liquids is shown by increasing tendency to 'slugging' at high viscosity.

Mixing in fluidized beds has been studied by E. R. Gilliland and A. E. Mason.[21] From experiments with a part-heated and part-cooled tube it is shown that in general the solid flows up the centre and down the wall. This would appear to explain the fact that on injection of helium part-way up the tube, its concentration below the injection point was higher at the wall than at the centre. In a study of pressure drop in vertical transport of solid by a fluid D. H. Belden and L. S. Kassel[22] have attempted to separate static and frictional effects of the particles. Deviation in the observed and calculated values may be due to ineffective end-corrections. Special emphasis is laid on the method of mixing the fluid and solid streams in a fluidized conveying system by L. Farbar.[23] The frictional component in fluidized solid flow is believed by O. H. Hariu and M. C. Molsted[24] to be negligible. From experiments with solid flow rates of 2 to 54 lb./sec./ft.^{2} and air velocities 12 to 40 ft./sec. the authors conclude that pressure drop can be regarded as that due to the carrier gas alone plus that due to the suspended solid; this deviates only slightly from the normal Stokes–Newton relationship. Deviations can be traced directly to energy absorption in the acceleration of particles in, for example, a pick-up section.

Heat transfer in fluidized beds is the subject of a paper by H. S. Mickley and C. A. Trilling.[25] Glass spheres were used in all experiments and tube diameter, bed depth and fluid velocity were varied as well as particle size. Heat-transfer coefficients of 10 to 120 B.Th.U./ft.^{2}/hr./°F. were simply correlated by a dimensionless factor and a term for bed density.

An unusual feature of the results is that with external heating an additional term involving the mass rate of flow of gas has to be introduced in the correlation. This is explained by the fact that the centrally-located heater used in experiments on internal heating prevents slugging in the bed. A slight deviation of results with small particles seems to indicate agglomerate fluidization.

L. K. McCune and R. H. Wilhelm[26] have examined conditions affecting mass transfer in fluidization by the dissolution of 2-naphthol (18-mesh—0·25 in.) in water. Correlation again involves terms similar to those employed in the Carman–Kozeny relationship and heat transfer is deduced by use of the Chilton and Colburn analogy. The authors point out that although mass transfer at the same Re is higher for fixed beds than for fluidized beds, the mass transfer per unit pressure drop is considerably higher under fluidized conditions.

Only three papers of the symposium deal with actual applications of fluidized technique. W. K. Lewis, E. R. Gilliland and G. T. McBride[27] describe experiments on the reaction of carbon dioxide with fluidized carbon at temperatures up to 2000° F. Although an equation is established for equilibrium of reaction the reactivity of different carbon samples renders it necessary to determine the constants for each individual sample and no general relationship can be given. W. K. Lewis, E. R. Gilliland and W. A. Reed[28] have studied the use of copper oxide supported on various solid media in the controlled oxidation of methane in a fluidized system and report that at 1700° F. 94% decomposition results with 92% efficiency of conversion to carbon monoxide and hydrogen. H. P. Meissner and H. S. Mickley[29] suggest the use of fluidized solids in trapping mists in gas. Sulphuric acid mist of 2 to 14 μ. can be removed with an efficiency of 90% but it would appear that an unnecessarily high pressure-drop would be involved in practical application.

Publications outside the symposium also show a distinct inclination towards studies of physical characteristics rather than applications of the process. M. Leva, M. Grummer, M. Weintraub and H. H. Storch[30] have extended their previous data for fluidization of irregularly-shaped particles by experiments on an iron oxide catalyst. Although the density of the material is much higher than sand particles previously considered, the equations already suggested by Leva *et al.* apply. An important point with respect to the scaling up of pilot-plant data stressed by the authors is the fact that as the diameter of a catalyst bed is increased the mass rate of flow of the fluidizing medium at constant space velocity decreases, with the result that maximum particle size for complete fluidization varies inversely as the cross-section of the catalyst bed. The irregularity of commercial catalysts gives rise to high expansion on fluidization. In a later paper, M. Leva, M. Weintraub and M. Grummer[31] describe measurements of heat transfer in fluidized sand and iron oxide catalysts. Results are correlated by equations with dimensionless groups involving the fraction voids in the same way as in the Kozeny relationship. At low velocities a heat transfer of 80 B.Th.U./ft.^{2}/hr./° F. is obtained and this value is relatively constant for varying density of solid and vessel diameter. These authors draw attention to the fact that

correlations based on quiescent beds appear to hold under slugging conditions. Channelling, on the other hand, leads to lower heat transfer. G. Kiddoo[32] refers to an increase of heat transfer in fluidized systems of 5 to 50 times that obtained when gas alone flows through the system; this optimistic comparison does not appear to take into account the very large change in pressure-drop involved. J. D. Parent, N. Yagol and C. S. Steiner[33] find that fluidized beds of varied-size particles are more homogeneous than beds formed with particles of constant size. Fine particles cohere and large particles give rise to a slugging tendency. In an article in which he stresses the importance of voidage and shape factor in flow through granular materials, M. Leva[34] plots fractional voids against the ratio of particle diameter r to tube diameter R for a variety of materials and shapes. An unusual feature is that there appears to be no tendency for the fraction voids to reach a constant value at low r/R ratios and in two cases the reverse occurs.

J. C. Dart, R. T. Savage and C. G. Kirkbride[35] give results of reaction-rate measurements in catalyst regeneration, and M. S. Dimitri, R. P. Jongedyk and H. C. Lewis[36] claim higher yields and ease of control in carbonization of hardwood sawdust by fluidization. A patent[37] has been granted for the use of a water-cooled air-fluidized bed of iron oxide in conversion of hydrogen sulphide to sulphur in a single stage.

J. M. Coulson[38] has carried out experiments in which a number of geometrically perfect-shaped but random-packed materials were used in a single column through which oil was passed, in efforts to establish equations for pressure-drop in static beds. The author critically examines the work of Chilton, Rose, Blake, Carman, Koseny and others, and reduces their equations to comparable states. He concludes that the Brownell and Katz correction factor for packing and shape variations is difficult to apply and that the Rose and Carman equations deviate at low voidage. The author recommends the use of the Blake equation with an additional orientation factor. Unfortunately, this term can only be established approximately by experiment. It would appear that as most packed beds consist of irregularly-shaped particles orientation can have only minor effect and the Blake equation should be effective for these in its present form.

Heat transfer

There have been fewer publications during the past year on the more fundamental aspects of heat transfer. R. E. White[39] has studied the condensation of Freon-12 on highly polished nickel tubes suspended horizontally in a vapour space. Values approximately 13% lower than those predicted by the Nusselt expression for condensation may be due to the extreme difficulty of obtaining any constant liquid film behaviour on a horizontal tube. J. C. Chu, R. K. Flitcraft and M. R. Holeman[40] have carried out a careful study of heat transfer in condensing vapour. They draw attention to the difficulty of ensuring completely non-turbulent flow in the liquid film, and they show that for benzene, toluene and ethyl acetate at various pressures but constant total heat flux the Nusselt expression is effective. Deviation at high rates of heat transfer

are attributed to turbulence in the liquid film. From a mathematical analysis the authors conclude that the heat transfer should vary inversely as the cube root of total heat flux. Their results for benzene and ethyl acetate confirm this but for toluene heat transfer varies directly with the cube root of heat flux. A. D. Davidson[41] finds that difficulties in application of the Nusselt equation for turbulent flow in heating and cooling are traceable to ineffective evaluation of the film viscosity. Davidson also stresses the errors which may occur in assuming any regular liquid film behaviour in condensation. D. Q. Kern and W. van Nostrand[42] find that in heating fatty acids the Sieder and Tate equation is only effective when an additional term involving the ratio of the viscosities of the wall film and main body of the liquid is introduced.

Three papers read before the Institution of Chemical Engineers and the Low Temperature Group of the Physical Society deal with heat transfer problems associated with liquid oxygen production. M. Guter[43] reports results of measurements of heat transfer in condenser-evaporator tubes similar to those used in Linde–Frankl plants. The estimated heat transfer under plant conditions is 400–600 kg.-cal./m.^{2}/hr./° c. Preliminary experiments in an apparatus similar to the commercial condenser but fitted with only 1–3 tubes are described. Nitrogen was boiled by an electric immersion heater and condensed inside the tubes, the heat transfer being measured by the rate of evaporation of liquid oxygen surrounding the tubes. With a single tube closed at the upper end, inert gas was found to collect and it greatly reduced the transfer rate. The advantage of increased surface in tubes of small diameter was offset by priming which set an ultimate limit to the heat transfer rate. 'Belling' the tube ends was found to reduce priming. With a number of tubes and a header priming was less troublesome, as one tube acted as a downtake; this suggests that it would be advantageous to provide proper liquid-sealed downtakes. Heat transfer rates of 1100 kg.-cal./m.^{2}/hr. have been obtained with a temperature difference of 1° c. G. G. Haselden and S. Prosad[44] have measured film transfer coefficients in the condensation of oxygen and nitrogen on the external surface of a single vertical tube cooled internally with the liquids. Recessed thermocouples were used to measure the tube surface temperature. Results agree with those predicted by the Nusselt expression. In a study of heat transfer to boiling liquid oxygen and nitrogen G. G. Haselden and J. I. Peters[45] used a rotatable electrically-heated horizontal cylinder with embedded thermocouples to measure its surface temperature. They find that ageing affects the efficiency of the heater and results are not easily duplicated. Consideration of the effect of maximum bubble pressure and work of bubble expansion yield no useful correlation. For high efficiency in liquid-oxygen plant the problem is invariably that of securing high heat transfer at very low temperature differences. H. Bliss and B. F. Dodge[46] stress this in a review of a number of possible cycles in gas liquefaction plant. They conclude that substantially pure oxygen should be capable of production with an energy expenditure of 0·15 h.p./lb. gas and 0·5–0·6 h.p./lb. liquid. Most existing plants have nearly twice this consumption, but the Linde Company claim that most up-to-date plant will operate with a power consumption of 0·194 h.p./lb.

W. H. McAdams, W. E. Kennel, C. S. Minden, R. Carl, P. M. Picornell and J. E. Dew[47] have extended the study of heat transfer to boiling liquid by the single-wire technique. The latest experiments have been carried out with an electrically heated tube 0·25 in. diam. supported in pyrex tubes of various diameters, through the annulus of which degassed water was pumped at velocities from 1 to 12 ft./sec. In the range where no bubbles were formed the results are correlated by the Sieder and Tate formula; in the boiling range the critical temperature difference is given by $\triangle t_{sat} = t_w - t_{sat}$, the difference in the wire temperature and saturation temperature of the water. The heat flux per unit area is then equal to $k(\triangle t_{sat})^{3.86}$, where k is a constant dependent almost exclusively on the quantity of dissolved gas in the water, and varying from 0·074 to 0·19. The effect of pressure, subcooling, liquid velocity and dimensions of the annulus on the rate of transfer is negligible. Peak densities of heat flux of 2×10^6 B.Th.U./ft.^{2}/hr. are recorded and high-speed photographs show that thermal destruction of the heating tube is due to the formation of a continuous film of vapour over the surface. Peak flux is related to water velocity and degree of subcooling but is independent of pressure.

M. Blackman, A. Egerton and E. V. Truter,[48] from experimental measurements of emissivity of various metallic surfaces conclude that very thin films of oxide have a distinct effect on rate of heat transfer by radiation; electrical conductivity measurements do not yield comparable results. In a study of the thermal transmission of dry metal-to-metal joints, N. D. Weills and E. A. Ryder[49] find that applied pressure results in a linear increase in conductivity for steel and exponential increase for aluminium and bronze. Oil-filled joints have approximately half the resistance of dry joints.

J. Leyland[50] discusses the methods available for large-scale water cooling. Modern concrete hyperbolic cooling towers will cool 6×10^6 gal. per hr. through a temperature range of 20–30° F. with low draught requirements. For cooling below the ambient dew-point partial evaporation under reduced pressure is effective. Economic points in the selection of cooling processes are discussed. The use of a general term for the 'efficiency' of a heat exchanger has been recommended by P. Grassman[51] and by Kühne.[52] Glaser[53] draws attention to the fact that a general efficiency based on rate of flow, pressure drop and heat transfer can have only limited use, as these features may have different degrees of importance in specific processes. The use of a term 'efficiency' as applied to heat exchangers is clearly of doubtful justification.

The heat pump continues to excite much interest. Its use in evaporation and drying is recommended by F. Joder[54] and D. Wittenberg.[55] These authors discuss the conditions conducive to economic application and show that rising cost and lack of fuel is making this process valuable in many instances. Its use in Germany is not economical according to A. Demski[56] because of cheap and adequate supplies of low grade fuels such as lignite. The largest heat pump installation in the U.S.A. is described by J. D. Krocker and R. C. Chewning.[57] This is used for air conditioning and is rendered economical by the necessity in this instance of a high cooling capacity in addition

to the heating requirements. Heat is drawn from water of two wells at 62·5 and 64·5° F. and some heat is recovered from exhaust ventilating air. Freon is used as the pump fluid and no auxiliary heating is provided. Details of a plant for concentration of fruit juices on the heat pump principle are given by T. Mitchell.[58] Ammonia is used in the pump, shell and tube exchangers being used for both heater and condenser. The evaporation is conducted at 50–70° F. under vacuum, so that thermolabile compounds are not destroyed. Although no critical examination of the economics of the process is available, it clearly offers a simple method of utilizing the low-potential heat in the condenser and should reduce the cost of evaporation markedly.

Apart from patent literature there is little published on heat transfer in finned tubes. L. Cohen and R. Jessel[59] have studied heat transfer conditions in a gas-fired water heater. In accordance with previous workers they show that no simple proportionality exists between the area of metal in a transverse-finned tube and its heat transfer. They present empirical equations for calculating the heat transfer from the results of experiments in which the gas and water velocities and temperatures were varied, and the fin thickness and arrangement of tubes altered.

Although the gas turbine is at the moment competitive with steam turbines only for electrical power generation in small installations, O. A. F. Munzinger[60] points out that it should find immediate application in auxiliary systems. A patent[61] has been granted for its use as an expansion engine in 'let-down' of high pressure gas from an organic synthesis. The expanded gases are scrubbed to remove the required product of the chemical reaction and power from the turbine is used for compression of the re-cycle gas. It is claimed that approximately 20% of the initial pressure energy is available as a net excess. Another patent[62] deals with the application of a gas turbine in a boiler plant in which the fuel is burned in a pressure furnace at 300 lb./sq.in., the gases expanding through the turbine to stack.

An ingenious ice-making machine is described by J. R. Watt.[63] By virtue of the low shear-strength of a steel and ice junction, an ice cone can be forced from a long truncated conical chamber (cooled externally by direct Freon refrigeration) by a ram mechanism at the narrow end. The chamber is filled with water and refrigeration started. The ram mechanism then operates at intervals of about 25 sec. to raise the block a short distance. Water from a feed ring at the top of the cone fills the interspace and this is frozen during the following 25 sec. Heat transmission is not reduced by passage through any large mass of ice and high efficiency and lower handling costs result; the continuously extruded block is simply cut as required.

Mass transfer

Distillation

Progress has been made in the prediction of thermodynamic properties of organic compounds on the basis of molecular structure. M. Souters, C. S. Matthews and C. O. Hurd[64] have evaluated heat capacities, heat content and entropy and heat of formation of a wide range of hydrocarbons on the assumption that similar structural groups make the same

contribution to thermodynamic factors irrespective of the molecule of which they form a part. The authors tabulate results of calculated heat capacity and heat content from − 250 to 3000° F. and heats of formation and entropy from 300 to 2000° K. That the method is effective is proved by the fact that over the wide range of temperature the results agree to within 3% in all cases. The chief difficulty in applying the method is in deciding for an unclassified compound the exact mode of translational, rotational and vibrational motion to be taken into account. Comparison with molecules of known characteristics is recommended at this stage of the calculation. A less fundamental approach to the same problem is made by J. L. Franklin.[65] He evaluates the effect of various groups on total heat and free energy from a study of experimental results on homologous series; various correction factors are involved but deviation from ideality has less effect and the method lends itself to the evaluation of thermodynamic properties of compounds other than hydrocarbons.

Attempts are still being made to produce simple linear graphs of equilibrium conditions by the use of non-linear reference scales. D. F. Othmer and R. Gilmont[66] show that, provided the reference scale is derived from a substance of similar but known characteristics, a fairly linear graph may be obtained. The main defect of such methods is usually failure to take into account some critical factor such as polarity. W. F. Rush and B. W. Gamson[67] emphasize this in deriving equilibrium relationships by a development of the McLeod equation. Deviations from their equations are in many instances directly proportional to the dipole moment of the substance.

D. S. Sherwin[68] has derived a simple approximation for constant enthalpy plate-by-plate computations on the basis that the enthalpy of liquid molal overflow is small compared to that of the rising vapour. A more accurate solution is presented by E. Kirschbaum.[69] An example calculation of Underwood's solution for multi-component distillation is given by R. V. Bailey and J. Coats.[70] M. W. Hall and E. L. Piret[71] have extended their investigation on the distillation of formaldehyde–water and –alcohol mixtures. Vapour density measurements confirm the presence of methylene glycol and hemiformal of the alcohol in the liquid phase, but in the vapour phase dissociation is almost complete. During vaporization the glycol decomposes readily to yield formaldehyde and water, and condensing formaldehyde dissolves in the water present but is not rapidly reconverted to the glycol. The vapour–liquid equilibrium is modified by the chemical reaction rate, resulting in formaldehyde concentration in the vapour phase.

O. G. Dixon,[72] in a series of articles, discusses the critical factors in close fractionation in laboratory columns. The author favours packing with gauze Lessing rings and from exhaustive measurements on the fractionation of 20% *n*-heptane–80% methyl*cyclo*hexane concludes that the factor of greatest importance in small-scale distillation is maintenance of a continuous film of liquid reflux over all parts of the packing. To obtain this the boiler is first overfilled and boiled rapidly to wet the packing by frothing, or is brought about by partially obstructing the flow of vapour at the base of the column. This may be effected by a

magnetically-operated valve which is partially closed at the beginning of a run until flooding is complete. As would be expected highest efficiency is obtained with the finest gauge of wire gauze. Increasing vapour velocity leads to lower fractionating efficiency, higher pressure drop and higher dynamic hold-up. Columns with gauze-ring packing have shown an efficiency of 84 theoretical plates per ft. and 50 plates per ft. is normal for a column 0·5 in. diam. and 1 ft. long with 1/16 in. rings operated at a vapour velocity of 0·3 ft./sec. To prevent heat loss from the column Dixon uses a loose-fitting oil-filled jacket maintained at about 10° C. above the boiler temperature. An apparatus suitable for close fractionation of 10–20 ml. of liquid is described, and graphs of cuts from a test mixture given.

E. A. Coulson, J. L. Hales and E. F. G. Herington[73] discuss the effect of varying volatility-ratio in estimation of the efficiency of fractionating columns. They reiterate the fact that variation is reduced by utilizing a mixture containing only a small proportion of one constituent in a second. They propose the use of dilute solutions of thiophen in benzene for column performance measurements. This mixture is suitable for columns of up to 65 plates and the estimation of thiophen can be conducted colorimetrically. R. T. Fowler[74] describes a modified equilibrium still in which the liquid phase sample is taken from a so-called Cottrell pump : this is in fact a liquid trap in contact with the vapour. As the author points out, equilibrium stills tend to become more complicated with each successive modification and the prevention of spurious condensation becomes more and more difficult. A. G. Crawford, G. Edwards and D. S. Lindsay[75] draw attention to the fact that complex equilibrium stills with many stopcocks are unsuitable for use with organic solvents and recommend a simple modification of the Othmer still with no stopcocks. From measurements of vapour pressure and equilibrium compositions of ethylene and methylene dichlorides, W. Davies, J. B. Jagger and H. K. Whalley[76] conclude that this represents an ideal mixture with respect to Raoult and Hildebrand laws. Their equilibrium measurements were conducted by simply condensing the first 10 ml. of vapour from the distillation of a large volume of the liquid mixture. Deviations may have been self-correcting as the analysis of the mixtures appears to have been carried out by the boiling-point method. F. H. Garner[77] draws attention to the variation of data obtained in different equilibrium stills by referring to results published for nitrobenzene–alcohol mixtures. The Othmer still yields erroneous results and one similar to that suggested by Fowler is recommended.

The search for an ideal packing for fractionating columns continues with unabated vigour. A. W. Fisher and R. J. Bowen[78] find that McMahon packing shows less dynamic hold-up variation with boil-up rate than Berl Saddles. The H.E.T.P. is 2·8 to 4·5 in. They draw attention to the errors which may arise by the use of the Fenske relationship even with an almost ideal mixture such as benzene–ethylene dichloride, and they revert to the McCabe–Thiele technique for evaluating column performance. M. R. Cannon[79] suggests the application of 'protruded metal' as split cylinders for column packing. This is metal punched with 1024 holes/in.^{2} in such a way that the edges of the holes

protrude. The material is said to be easily wetted by capillarity and the holes do not seal with liquid. No preflooding is required and high efficiency is claimed though no actual data are given. H. J. John and C. E. Reyberg[80] suggest that a regular packing similar to that of Stedman is more simply fitted by inserting the gauze plates one by one and forcing each plate down with a spring washer which presses against the column wall. This should provide a better wall seal than that of Stedman packing (the defect of which is widely recognized) but more operations are involved than in the fitting of Stedman plates, particularly if the latter are mounted on a central control wire. As with the Stedman packing the efficiency is high only at low reboil rates, i.e. near the wetting failure point. It is noticeable that none of the packings described show H.E.T.Ps. of even the same order of magnitude as those obtained in Dixon's experiments with plain gauze rings, and it would seem that conditions of operation have a greater bearing on efficiency than the type of packing.

H. S. Kemp and C. Pyle[81] have carried out an investigation on the effect of hydraulic gradient on the pressure-drop and performance of bubble-cap trays. The effect of spacing, number of rows of caps and skirt clearance are reported. Their results prove the necessity of adequate down-flow arrangements for high efficiency. Another paper dealing with the computation of pressure-drop over bubble-cap trays is given by A. C. Eld.[82] C. O. Rhys[83] suggests that hold-down bars on industrial bubble-cap columns has a substantial effect in reducing throughput; this author also stresses the importance of downcomers and careful cap arrangement in fractionating columns.

The preparation of pure methyl*cyclo*hexane from a straight-run heptane fraction of petroleum by distillation with an extractive agent is described by J. Griswold and J. W. Morris.[84] Complete details are given of the plant and operating conditions. G. T. Atkins and C. M. Boyer[85] show that the McCabe–Thiele diagram can be effectively applied in extractive distillation problems. Plate-by-plate calculations for total reflux are first made for the mixture and the results for the concentration of the lowest boiling component in the complete mixture plotted in the usual way. The authors have applied the method in the separation of butylenes and butanes using acetone–water as the extractive agent. By its application the authors were able to calculate reflux ratio changes necessary for varying feedstocks. R. F. Marschner and W. P. Cropper[86] in the course of a study of the distillation of a petroleum fraction have observed the presence of a large number of toluene azeotropes. In subsequent investigation they show that the boiling point of the azeotrope and its composition are related to the boiling point of the pure hydrocarbons. A linear relationship is obtained when the boiling points of the hydrocarbons are plotted against the difference between 111·6 and the azeotrope boiling point.

Absorption and extraction

R. P. Whitney and J. E. Vivian[87] have examined the film transfer coefficients for absorption of sulphur dioxide in water flowing through a packed tower. The liquid film transfer coefficient is found to vary in the normal way with the 0·8 power of liquid velocity. In correlating

gas film coefficients the authors find that a term involving the 0·25 power of the liquid velocity is necessary. Deviation from the Sherwood relationship is believed to be due to low hydrolysis and diffusion rates. No results are given for measurements of the diffusivity or hydrolysis rates and no absolute conclusion is possible. C. R. Wilke[88] suggests a simple method for the approximate evaluation of diffusivity on the basis of the Eyring hypothesis that liquid diffusion depends on viscous flow of solute through 'holes' in the solvent. He defines a solvent factor to correlate diffusivity in different solvents; the absolute diffusivity is then directly proportional to the relative molecular volumes of solute molecules and inversely related to the viscosity of the solvent. Sufficient data are not yet available to confirm the relationship but it provides at least a simple method of determining the order of the diffusivity.

W. H. McAdams, J. B. Pohleny and R. C. St. John[89] describe experiments on mass and heat transfer in air flow over wetted Raschig rings in a 4-in. diam. tower. These authors also suggest the inclusion of a liquid velocity term in the gas velocity–heat-transfer relationship, and draw attention to errors which may be introduced by the assumption of negligible liquid film resistance in the transfer mechanism. This may represent 20–40% of the total resistance. An equation is derived for tie-line slope between operating and equilibrium lines in cooling tower calculations. This takes into account the effect of liquid film resistance. L. E. Hutchings, L. F. Stutzman and H. A. Koch[90] find that a 6% scatter in their results for gas film transfer coefficient in the absorption of acetone from air by water washing in a Raschig ring-packed column is eliminated by the introduction of a liquid velocity term similar to that suggested by McAdams *et al.* W. S. Norman[91] favours a more theoretical approach to mass- and heat-transfer problems on the grounds that it yields relations more widely applicable than empirical methods such as dimensional analysis. Experiments on distillation of ethanol–water mixtures in a wetted-wall column yielded mass transfer results which are effectively correlated by the Chilton–Colburn equation. Introduction of a wire spiral in close contact with the column wall doubled the mass transfer and quadrupled the pressure drop. This non-proportionality of pressure drop and mass transfer is explained by 'form drag,' which represents loss by turbulence in the wake of the mass-transferring surface. Equations derived on this basis are applied to the results of experiments by other workers with a variety of absorbents and packings. Satisfactory correlation is obtained in the case of spherical packing but not with more complex shapes. The author suggests that deviation may be due to incomplete wetting in these cases. In a study of mass and heat transfer by measurement of the rate of water evaporation from porous packing, R. G. Taecker and O. A. Hougen[92] find that correlation can be effected by the use of Krevelin and Hoftijzer's equations. They propose some variation in the constants for different types of packing, the essential terms being, mass rate of flow, viscosity and the superficial area of the packing. Ring-packing gives lower transfer rates than Berl saddles—an effect attributed to low transfer efficiency associated with the inner surface of the rings. The application of some kind of shape factor would appear to be necessary for variations of this type.

H. J. Hibshman[93] suggests that the product of 'separation selectivities' in distillation and liquid–liquid extraction is equal to that for vapour–liquid extraction. This should enable liquid–liquid extraction data to be predicted from vapour–liquid equilibrium measurements. From a limited number of measurements the author postulates extraction constants for some systems but no experimental verification of the constants is given.

E. G. Scheibel[94] describes an extraction apparatus consisting of a column with a series of short-packed sections with alternate sections of free space fitted with agitators connected to a central drive shaft. In counter-current extraction tests on the separation of *o*- and *p*-chloronitrobenzene in a 1-in. diam. column, stages consisting of 0·2 in. stirred section and 2-in. wire packing yielded virtually complete equilibrium stages. A larger unit is in course of construction. The author stresses the errors which may arise in the use of distribution coefficients calculated from liquid–vapour relationships. Calculations based on activity coefficients showed that ethanol could be separated from methyl ethyl ketone by a water–paraffin mixture in 7·4 theoretical stages, whereas the separation was effected in a 7-stage experimental extractor. Fine wire or glass helices are recommended by H. L. How and N. W. Franke[95] as a packing for the promotion of droplet formation in liquid-liquid extractors. H.T.Us. of as low as 0·2 ft. have been obtained.

A. N. Hixson and L. Garwin[96] show that although octanol is a solvent for cobaltous chloride, it is not suitable by itself for the extraction of the salt from water. In presence of added chloride ion in the aqueous phase extraction with this solvent is possible; hydrochloric acid or calcium chloride are suitable additives. T. G. Hunter and T. F. Brown[97] have compared the liquid-liquid extraction and low-temperature processes for dewaxing mineral oil. They conclude from experiments on the removal of cetane from a number of hydrocarbons and mixtures with aniline, that the process is less efficient than the freezing method, a larger number of extraction stages being necessary to give equivalent residual wax in the oil.

O. F. Gee and W. H. Shearon[98] describe a full-scale plant for the production of carotene and chlorophyll from alfalfa by absorption on active charcoal of a hexane extract of the grass. The adsorbed products are eluted with hexane to recover the carotene. Xanthophyll is obtained by elution with hexane containing a small fraction of alcohol. Back-elution with benzene–*iso*propyl alcohol removes the chlorophyll from the charcoal bed. The carotene fraction is purified by a second adsorption and elution; complete details of the method of dealing with intermediate fractions are given. J. M. Beveridge, A. J. Sweetman and F. D. Rossini[99] in a series of experiments on the adsorption on silica gel of a gas–oil fraction of petroleum have obtained three distinct fractions: paraffin–*cyclo*paraffin, mononuclear aromatics and polynuclear aromatics. With a wax fraction (aromatic-free) a separation of the paraffins and *cyclo*paraffins was obtained. The effects of column diameter, length, change in temperature and size of charge are reported. The graphs of composition of the column effluent are analogous to batch distillation curves, and cuts are in general well defined.

Filtration and gas-cleaning

In a paper on practical features of filtration K. S. Meyer[100] regards filter-cakes as falling into three more or less well-defined classes. A free-filtering cake with particles arranged in an orderly manner and size increasing with distance from the filter cloth gives good filtration rate but may not yield fully clarified filtrate. The second type—porous cake consisting of a mass of large particles with a surface dressing of finer particles—exhibits a tendency to choke but gives a clear filtrate. In the final group, which the author describes as 'double-layer' cakes, the fine solid is randomly distributed throughout the mass and rapid choking always results. In all cases the application of filter aids and careful control of pressure will increase the overall rate of clear filtrate production. Emulation of the first type of cake in disc filter pads by the use of papers or paper pulp with the lowest pore size near the exit surface is the subject of a patent.[101] Patents[102,103] have been granted for two novel filter media : the use of a cooled filter-bed of finely-crushed ice for the removal of suspended matter in fruit juice, and a sintered mass of metal spheres of controlled particle size. The latter is described in some detail by J. W. Lennox and G. Brewer.[104] The metal is rendered spherical before sintering by atomization in an oxy-gas flame, after which it is classified. Photographs of the sintered product show the great regularity of the bed of close-packed spheres. The bed is free from acute projections into the filtrate channels, so that particles of solid smaller than the filter pore size pass readily through the labyrinth without sticking, and tests show that the material is almost ideal as a size-discriminating filter. The mechanical properties are similar to those of porcelain and it can be produced from a wide variety of metals and alloys.

L. E. Brownell and G. B. Gutz[105] present a useful paper on the practical estimation of exhauster requirements for rotary-vacuum filters. The relationships in two-phase flow by Brownell and Katz have been simplified by numerous assumptions and approximations. A voidage of 0·4 is taken as applying to all filter-cakes, and to aid in integration of equations over the filter cycle, laminar flow is assumed. With air flow during the drying portion of the cycle, flow is markedly turbulent and a simple graphical correction is used here. Graphs are presented which enable the various factors in the equations to be evaluated from a knowledge of well-established physical constants of the solid, filtrate, air and water. The results must be very approximate but the method has the advantage that it does not involve a knowledge of unusual physical constants of the materials.

R. D. Hoak and C. J. Sindlinger[106] point out that filtration may be simplified by strict attention to precipitation conditions. Difficulties in the filtration of a precipitate of iron salts from pickle-liquor are due to the gelatinous nature of the solid. Effective agitation and controlled air oxidation during the precipitation produce an easily filterable solid, obviate the need for filter aid and reduce the bulk of the final cake. N. F. Chamberlin, J. A. Dinwiddle and J. L. Franklin[107] give an account of a qualitative study of the effects of crystal aids in the crystallization of wax from liquid propane. Photomicrographs were made with an ingenious polarizing microscope assembly which permitted examination

of the system while under pressure. A full description of the apparatus is given and photographs of the compacting of crystal agglomerates in presence of a small quantity of asphalt are presented. With increasing asphalt content, smaller but still compacted crystals result and a study is being conducted on the effects of the butane-soluble and -insoluble fractions of the asphalt in an effort to obtain a colour-free crystal aid.

Sand filters are usually employed in clarifying natural waters and there is little opportunity to modify the filtering properties of the suspended solid. Back washing is effective only in certain cases and the bed has to be frequently renewed. Two patents[108,109] describe devices to simplify washing and prolong the life of the filter-bed. Both depend on the injection of air and water at or below the sand level to gently agitate the bed surface during backwashing—the sludge being removed through a discharge pipe just above the bed surface.

A. J. ter Linden[110] has determined the most efficient shape of a cyclone from measurements of the effect of variation of each of its principal dimensions. The author proposes the use of multiple small cyclones in parallel for the removal of fine dusts from gases. This leads to high-power requirements and cyclones become uneconomical with very small particles. M. W. First and L. Silverman[111] derive equations for separation efficiencies of cyclone separators on the basis of Stokes' law, and for pressure drop from the velocity distribution, expansion and contraction losses in the system. The equations enable an estimate to be made of the degree of separation of any particular size of particle. It is doubtful whether Stokes' law will apply satisfactorily to a cyclone except at low velocities and reduced solids loading.

In considering the chemical engineering problems associated with the dolomite–sea-water process for magnesia, H. W. Thorp and W. C. Gilpin[112] stress the difficulties of removing dusts containing magnesium oxide, sodium and magnesium chlorides and sulphates from the flue gases of the rotary kiln used to dehydrate the final product. This dust in stack gases was responsible for the deposition of a fog over a wide area about the factory. Removal of 95% of the dust has little effect on the fog-producing qualities as the remaining 5% contains the finest and most potent fog-producing particles. Electrostatic precipitation is the only process capable of giving the necessary efficiency (99%) and the hygroscopic nature of the dust renders ineffective the collection of dust by 'rapping' the precipitator wires. A precipitator which is automatically switched off and sprayed with water at intervals is proposed. Before precipitation the gas is to be cooled to 35° c. by water sprays, but it is not clear how this gas will behave in the stack. The untreated gas (dew-point 70° c.) enters the stack base at 350° c. and the change will mean altogether different draught and corrosion conditions. H.M. Chief Inspector[113] reports an investigation into fog-producing dust in the exit gas of magnesia kilns and recommended the replacement of a liquid scrubbing system by electrostatic precipitators. A similar nuisance produced by effluent gases from a melting plant handling aluminium scrap was traced to the presence of sodium chloride in the gas.

The effect of dielectric constant of a solid on its behaviour in electrostatic precipitation is the subject of a report by F. Fraas and O. C.

Ralston.[114] With barium strontium titanate, which behaves as a good electrical conductor, charging is believed to be due to concentration of the field about the particle. Special qualities of a substance that may affect the ease with which it releases electrons are discussed but no definite conclusions given.

An interesting principle is embodied in a patent[115] filter for removing finely-divided solids from a gas stream. This consists of a felted fabric element coated with a highly insulating synthetic resin, which becomes electrically charged with the passage of the gas and thereafter behaves like a narrow-passage electrostatic precipitator, collecting dust particles much smaller than the pore diameter. The mode of action of polystyrene-coated filters of this type is discussed in a paper by R. Weber.[116]

An abbreviated review of recent literature on filtration is given by S. A. Miller.[117]

Evaporation and crystallization

A striking development in the field of evaporation is the new and pronounced interest in submerged combustion. A patent has been granted to N. Swindin[118] for an improved burner of this type and in a later paper Swindin[119] describes the recent advances in submerged combustion burners. In a well-designed burner the waste gas leaves the surface of the evaporating liquid only a few degrees above the liquid temperature sensible heat utilization at this stage is virtually 100%. Difficulties with deposition of solids on the burner tip in the evaporation of pickle-liquor in experiments with 2-in. diameter burners are almost non-existent when 7-in. diameter burners are employed. An ingenious system of pre-evaporation devised by the author recovers a large fraction of the latent heat in the gas–vapour mixture leaving the main evaporator. When the mixture is passed at velocities of the order of 200 ft./sec. through a series of tubes in a horizontal bank and over which the feed liquor runs contrary to a controlled air supply, the latter also leaves nearly saturated with water at approximately 40° C. By careful adjustment of the air supply at this stage heat transfers of 150 B.Th.U./ft.^{2}/hr./°F. can be obtained and the performance coefficient for the whole system raised to 1·62, a value comparable with double-effect evaporation. These principles have been embodied in the design for an evaporator to produce 2 tons/hr. 70% sulphuric acid from 35% feed. The heating contact time is only 15 minutes. Swindin draws attention to the value of submerged combustion in the evaporation of 'bittern,' the liquid remaining after calcium and magnesium salts have been precipitated from sea-water. Because of its froth-forming properties considerable difficulty arises in its concentration and rates of evaporation are low. With submerged combustion the evaporation can be conducted at 10–12 times the maximum rate by other methods and no frothing occurs.

E. M. Burdick, C. O. Anderson and W. E. Duncan[120] draw attention to the advantages of submerged combustion in the concentration of citrus juice wastes. In conventional evaporators scale formation is such as to reduce the evaporative capacity 50% in 8 hr. and foaming is difficult to control. In a submerged combustion plant single burners are capable of delivering heat at the rate of 4 to 5 $\times$ 10^6 B.Th.U./ft.^{3}/hr. and descaling

is only necessary at intervals of about 70 days. No foaming occurs and the product liquor is more nearly sterile than that produced by the older method and can be stored for longer periods without spontaneous fermentation. Details of safety devices and controls for the mixed gas–air burners are described. The authors foresee much wider application of this form of evaporation.

J. Coates[121] proposes a short method for calculating total surface requirements in multiple-effect evaporation based on average values of heat-transfer coefficient, temperature difference and thermal constants of the liquor. The method makes use of a number of simplifying assumptions such as the linearity of heat-transfer temperature and other relations and would appear to be useful only when the heating area is the same in all effects. Results within a few per cent. of the more elaborate methods are claimed, but the method is rather inflexible. F. M. Hildebrandt[122] describes a laboratory-scale glass evaporator capable of easy modification for forced circulation, with internal or external callandria, and useful in evaluating the scale-forming qualities of liquors. He gives results of evaporation of molasses stillage-liquors containing calcium sulphate and suggests scale-preventive measures. A patent[123] has been granted for the use of liquid-repellent films such as silicones on the internal surface of glass apparatus to prevent 'bumping.' It is claimed that heat-transfer rates are increased by such application. A patent[124] on the prevention of foaming in the evaporation of colloids, is based on the addition of mixed polymers of ethylene glycol, hydrogenated castor-oil and paraffin wax partly saponified with potassium hydroxide.

C. M. Loucks and C. H. Groom[125] discuss the cleaning of heat-exchange and evaporator equipment with chemical reagents. The problem of removing mixed deposits may necessitate more than one reagent, and the addition of various inhibitors for hydrochloric acid is considered. Heat transfer through graphite and porcelain evaporator tubes is the subject of experiments reported by E. Kirschbaum.[126] Considerable improvement in strength, homogeneity and non-porosity has been effected in graphite equipment, and heat transfer compares more favourably with metal tubes than does porcelain.

A rotating drum evaporator for the removal of undesirable low-boiling constituents from edible oils is the subject of a patent.[127] The apparatus is described[128] as a horizontal steam-heated drum inside which rotates a smaller drum bearing longitudinal blades which carry the feed liquor over the internal wall of the jacket. Vapour generated at this stage is drawn off from the upper section of the chamber. The liquid then passes through ports to the internal drum where live steam is injected to complete the evaporation. The liquid is elevated through successive annuli by scoops fitted on the rotating drum until it reaches the centre-line where it overflows through a trunnion bearing to the exit pipe. The device is said to be applicable to foaming liquids and the scraping action of the blades prevents deposited solids from building up on the heating surface. The evaporation of liquids by direct use of their electrical resistance is claimed in a patent.[129] A series of electrodes are closely spaced so that when partially immersed, the liquid rises in the interspaces by capillarity. Current passed between alternate electrodes evaporates

the liquid. Patents[130] have been granted for the use of dielectric heating in evaporation. To avoid the danger of bubble formation and arcing between the electrodes the heating chamber is pressurized, the liquid being flash-evaporated in a second lower-pressure vessel.

The direct use of solar energy in evaporation is referred to by J. R. Callahan.[131] In the production of synthetic zeolite for water softening at a plant in California the mixture of silicates and aluminates is dried simply by spreading on a concrete surface outdoors. To obtain the desired grain size water is sprayed on the product when partially dry and cracking results. The initial mixture contains 95% water and on a 37-acre surface 25×10^6 lb. of zeolite per annum are produced. The drying cycle is approximately 5 weeks, the relative humidity being 5–10% and ambient temperatures up to 115° F. occurring in summer. Concentration of fruit juices and other heat-sensitive materials by freezing is arousing interest. A patent[132] has been granted for juice concentration by freezing to a solid mass and raising the temperature to recover the concentrated material. S. Kiesskalt[133] discusses the bearing of the Clausius–Clapeyron equation on the concentration of vitamin and hormone solutions by freezing out water at high pressures.

E. L. Pfeiffer[134] gives an approximate method for the calculation of dimensions of cooling towers. A patent[135] in respect of dampers for the control of air flow in natural-draught cooling towers refers to the increased entrainment of water droplets when the difference between the external and internal temperatures is too great. Entrainment varies as the sixth power of air velocity.

A. W. Bamforth[136] restates the conditions necessary for the production of large regular crystals on a commercial scale. The various modifications of the Krystal plant which permits its use as an evaporator, vacuum or cooling type of unit are described. Flow-sheets and plant details of the installation of a Krystal plant for 350,000 tons/annum ammonium sulphate are given. C. S. Grove and J. B. Gray[137] in a review of recent work on crystallization refer to the modern processes in use for the growth of large single crystals for optical and electrical purposes.

J. Whetstone[138] reviews the many methods which have been tried to reduce the hard-setting characteristics of ammonium nitrate. It is concluded that hard-setting is due to bridging of crystals by drops of solution formed in moist storage, followed by crystallization of the solution bridges. The author has examined the effect of various 'dusting' materials and shows that their reactions can be traced to their hydrophobic and hydrophilic properties. Aluminium stearate is an effective agent of the hydrophobic group which acts mainly by mechanically separating the particles of salt. Many substances, suitable from the point of view of setting properties, are excluded by virtue of their effects on the explosive properties of the ammonium nitrate. Addition of a trace of magenta to the magma completely alters the crystal habit, fine plate-crystals being produced under these conditions. These crystals have only weak adhesive properties and if the salt is dried in presence of magenta the superficial deposit of dye is active in producing plate crystals in the event of a crystal bridge forming under moist storage conditions. Magenta used in this way is found to have no effect on the

explosive qualities of the material. It is unfortunate that no method is available to predict what substances may be effective in changing crystal habit in this way, as there are many products where such a process would be advantageous.

Mixing

The results of experiments by A. N. Hoffman, J. B. Montgomery and J. K. Moore[139] on the efficiency of agitation in oscillating systems fill a decided gap in the data of mixing processes. To establish optimum conditions for agitation in shaking autoclaves the authors conducted experiments on the rate of hydrogenation of nitrobenzene in glacial acetic acid in a variety of cylindrical glass vessels oscillated longitudinally. The results show that for any particular stroke length there is an optimum shaking frequency. Maximum reaction is associated with the greatest stroke length. The effect of L/D ratio for the vessel is marked but no general rule is apparent here. For example, the order of L/D ratio for decreasing rate of reaction in a 500-ml. vessel half full is 6 : 1, 13 : 1, 8 : 1, and for a 1200-ml. vessel under the same conditions 8 : 1, 6 : 1, 13 : 1. It is unfortunate that no rule could be established in this case as it would have considerable bearing on the design of shaking autoclaves. The authors find, as would be expected, that a longitudinal movement of this kind is 3·5 times as effective in contacting the gaseous and liquid phases as a rocking motion. The effects of viscosity, density and surface tension would be of great interest but are not reported at this stage.

D. E. Mack and R. A. Marriner[140] have evaluated the effect of mechanical stirring on mass transfer measured by the rate of reaction of benzoic acid pellets with dilute sodium hydroxide solution. All their results can be correlated using a power constant for the propeller and the modified Reynolds number previously suggested—$NL^2\rho/\mu$. Changes in the level of liquid could be reconciled by the introduction of a power of the H/D ratio. All experiments were conducted under fully baffled conditions and although experiments were not extensive (e.g. ρ and μ were not varied) the results are well correlated by the suggested formula. It is surprising that such a heterogeneous system should lend itself to simple mathematical correlation. A similar study has been conducted by A. W. Hixson and M. I. Smith.[141] They measured the effect of stirring on the rate of transfer of iodine from water to carbon tetrachloride. The authors assume that the coefficient of distribution of the solute between the two phases is independent of concentration and that equilibrium is complete at the interface. Their equation for mass transferred in unit time is based on the ratio of the solvent masses and involves a term designated 'extraction coefficient.' The latter varies directly with stirrer speed but is not simply related to vessel dimensions so that scaling-up to larger-sized plant is not satisfactory.

R. D. Collins and M. P. Newby[142] have employed an infra-red gas analyser to study the mixing of air and carbon dioxide in a model open-hearth furnace. The results suggest that in conventional furnaces only slow mixing occurs and air may flow from the inlet to the outlet port by streaming along the furnace roof without oxidizing any combustible gas. Although the method is ingenious, it is difficult to emulate all the

effects of large-scale operation in a model furnace and the results must be viewed in this light.

K. S. Valentine[143], puts forward the view that simple baffled tanks fitted with stirrers are more effective than tower scrubbers for gas absorption, and particularly when the liquid absorbent may contain solids in suspension. By suitable design the agitators can be made to carry the gas down through the liquid and expel it under vertical baffles where the gas separates and passes to the next vessel for contact with counterflowing liquid. No details are given of power consumption.

Data on emulsifying devices are almost wholly confined to patent literature. Increased comminution in gear-pump homogenizers is claimed[144] by serration of the internal walls of the pump and discharge ports. A patent[145] emulsifier consists of a rotating multi-start threaded barrel running in a cylindrical gauze screen, the materials entering at the lower end and passing through the gauze to leave the apparatus near the top of the rotating mechanism.

The increased use of foams for fire fighting has promoted interest in foam stabilization. The use of a product produced by heating dried blood, or similar protein-containing material, with a heavy-metal oxide in alkaline suspension, is the subject of a patent.[146] A patent[147] has been granted for the use of polyvalent metal salts of similarly treated proteinoid material for the stabilization of air–water foams.

Progress in mixing processes during the past few years is reviewed by J. H. Rushton.[148]

Drying

There have been a number of notable articles in this field during the past year, especially on rotary kilns. S. J. Friedman and W. R. Marshall[149] in experiments on the hold-up in rotary driers used a model 1 ft. in diameter and 6 ft. long, which could be adapted to parallel and counter-flow operation, and the slope of which could be altered at will. From experiments with a wide range of materials they show that the average time of passage of a particle is directly related to the hold-up and length of the drier and inversely proportional to the feed rate, slope and 0·9 power of the speed of rotation. The introduction of 'flights' up to eight in number leads to increased hold-up; additional flights have little effect on the transit time. The effect of air flow is to increase or decrease the hold-up according as the flow is counter- or co-current, the effect being almost directly related to the air velocity and a function of the solid particle size. No simple relation is observed between air flow and dust carry-over except that beyond a distinct critical velocity there is a rapid increase in 'dusting.' Increased drum speed, as would be expected, increases dusting and low feed rates are conducive to a high degree of carry-over; the correlation of results with different solids is not satisfactory but the graphs which are presented should be useful in drier design.

In a later paper[150] the same authors go on to consider heat transfer in the experimental drier. To avoid errors due to simultaneous mass and heat transfer dry sand was used, and heat transfer measured by the rise in temperature of the solid. The methods of obtaining reliable

measurements of the sand temperature at various points in the machine are described fully. Heat transfer is found to be dependent on the 0·5 power of hold-up. Increasing the feed rate increases the heat transfer up to the point at which the flights are fully loaded. Feed in excess of this amount simply moves along the base of the drum and is not accompanied by any increase in heat transfer. Previous investigators have suggested that the heat-transfer rate varies as the 0·46 power of air velocity. The present workers find a variation of only the 0·16 power and suggest that the high value may be explained by uncorrected thermal losses and the use of a log mean temperature difference which is now claimed to be inapplicable in driers of this type. Increased speed of rotation is accompanied by a corresponding reduction in the hold-up and no change occurs in the heat transfer. Particle size has little effect. Reduction of the slope of the drier leads to higher heat transfer until a critical minimum slope is exceeded, when no further change occurs. The addition of two flights has a pronounced effect but becomes less marked as further flights are added. L. Vahl[151] stresses the fact that a knowledge of the effect of these variables is essential to ensure uniformity of product and as an aid in adjusting starting conditions in large-scale rotary driers.

D. W. van Krevelen[152] finds that particle size has a pronounced effect in the drying of granulated fertilizers and he reports that the drying rate of materials of this type is only about 1/50th of that of coal particles of similar size. In two papers D. W. van Krevelen and P. J. Hoftijzer[153,154] report detailed investigations into the drying of large granules. In primary experiments single granules 0·3 to 1 cm. diam. were suspended in a heated air stream and the rate of mass transfer estimated from the loss in weight, a torsion balance being employed in the measurements. With wet marl the usual constant and falling drying rates were observed and equations derived for the mass transfer. The authors conclude that the falling rate period of drying is best explained by assuming the granule to be composed of packed spheres, water finally collecting by capillarity at the points of contact. Drying is then characterized by evaporation of the water at these points followed by diffusion of the vapour to the granule surface and convective transfer into the gas stream. The equations derived on this assumption are well borne out by experiment. With a crystal-forming material (nitro-chalk fertilizer) the cycle is entirely different, a rapid decrease in rate at first giving way to constant but very low drying rate. This is shown to be due to the formation of a superficial crystal film 10^{-3} to 10^{-5} cm. thick, through which water from the interior must diffuse. The diffusion rate is estimated to be 1000 times lower than that of mass transfer through the gas film and therefore completely controls the overall rate of transfer. This rate is obtained in drying fertilizers in commercial rotary driers. With compacted granules similar to marl, commercial driers give a drying rate about 1/5th of that for the freely suspended material, and this rate varies as the 0·5 power of the rate of rotation. The product of residence time, speed of rotation, diameter-length ration and the tangent of the angle of inclination is thought to be a constant for all rotary driers and depends only on the number of 'steps' into which the drier is divided diametrically.

C. S. Rao and S. S. Dharmayya[155] report that dried leather and cardboard are effective desiccants for use in the storage of optical instruments. The properties of calcium chloride, calcium oxide and silica gel are compared from the point of view of rapidity of desiccant effect and capacity for water. The chloride has the highest capacity and the oxide the highest rate of absorption and a mixture is recommended for maximum efficiency. The advantage of silica gel is its non-corrosive nature.

The rate of mass transfer in the absorption of water with concentrated calcium chloride solutions in packed columns is the subject of a paper by E. F. Thurston.[156] He concludes that the effect of the gas film is predominant in the transfer mechanism.

E. F. Mactaggart[157] reviews the development of industrial driers over the last 50 years. Cleanliness in operation and simplicity of design and construction are the features stressed. A great variety of driers are illustrated and their salient points brought out.

C. W. Gordon[158] describes suspended-particle driers. A co-current drier in which the particles are circulated with gas at up to 1300° F. is claimed to be suitable even for inflammable materials because of the low time of contact. For filter-cake drying, addition of a proportion of dried cake to the feed permits the application of a similar drier. These driers are specially adapted to work in conjunction with a disintegrator, a large fraction of the drying being effected in the actual mill. The short contact time in these driers can be disadvantageous with certain materials and to obviate this P. Barr[159] suggests a controllable degree of re-cycling. He describes and illustrates some units of this type.

W. F. Bixby[160] describes the application of a modified Fourdrinier machine to the drying of rubber latex. This is capable of reducing the water content of the latex from 45 to 0·5% with a sheet speed of about 30 ft./min., the total drying time being 7–8 minutes.

The problem of heat transfer to a material drying under high vacuum may be solved in certain cases by the use of radio-frequency heating and a patent[161] has been granted for this process. R. L. Stephens[162] reports that only porous materials can be effectively dried by dielectric heating and C. A. Mann, N. H. Ceaglske and A. C. Olson[163] show that the mechanism of drying by radio-frequency is the same as by conventional systems of heating. They draw attention to the need for circulating air at a higher temperature than the heated solid to remove the water evolved. Organic solvents are less readily removed than water by this process. H. H. Chambers[164] discusses the uses of freeze-drying. Over and above the advantages in respect of thermally labile products, are the lack of shrinking and elimination of high concentration of product in surface layers which occurs in drying at elevated temperatures.

Size reduction

This is still one of the most empirical unit processes. B. Epstein[165] suggests that the breakage of a solid must be a stepwise process and capable of simple statistical analysis. Making two major assumptions, that the probability of breakage of a large particle is independent of its size and related only to the number of steps already completed, and that the number of pieces produced in a single fracture is independent

of the original size, it can be shown that the statistical distribution of sizes should approximate to a logarithmic form. The equation is limited in its application as it applies only to size reduction by shattering and no grinding or crushing process can be said to operate by this mechanism alone. J. N. S. Kwong, J. T. Adams, J. F. Johnson and E. L. Piret[166] have used an improved falling-weight method to study the fundamentals of the crushing process. The value of this work lies in the careful elimination of secondary effects. The material to be crushed was retained in a chamber between two anvils and compression was applied by dropping a steel ball on the upper anvil. Energy not used in crushing was absorbed in flattening aluminium wires, the work–deformation qualities of which were known. The aluminium also prevented 'bouncing' and obviated the correction usually applied for this. In crushing quartz, fluorite, labradorite and glass the graph of new surface produced against work done is linear and passes accurately through the origin. Permeability measurements were used in these tests to evaluate surface area.

S. H. Bransom and W. J. Dunning[167] propose a photoelectric method for estimating size distribution. The equations suggested are borne out in the case of cobalt-glass spheres. A distinct divergence with opaque white irregular particles is attributed to inefficient microscopy, the reference method used in all tests. Three correction factors of major importance to the photoelectric method—light scattering by non-black particles, equivalent radius of non-spherical particles, and a shadow distribution function—are difficult to evaluate and it would appear more logical to regard these with some doubt rather than the chosen experimental standard, in explaining divergence.

P. D. Blake[168] presents a critical review of the Heywood and Roller methods for evaluating surface area of fine powders. Concise descriptions of the methods are given and mathematically and experimentally analysed. The author concludes that the Heywood method in its simplified industrial form is prone to certain errors, particularly with respect to the evaluation of shape factors. Important measurements in the Heywood system are concerned with particles under 7 μ. and can only be conducted by laborious microscopic measurements. The Roller method is preferable, and by a modification of the equivalent size of particles from a geometrical basis to a statistical diameter, can be made to apply directly to the results of the hydrometer method of particle size determination. With this modification the values obtained are believed to be more reliable than those obtained by the original Roller method, and it can be applied with the results of only four measurements of size distribution in the material.

J. V. Hightower[169] draws attention to the advantages of wet milling in an article on corn processing. Dextrose and edible oil is made from corn by a new process where wet milling is employed at two stages in the manufacture. After steeping, the corn is passed in the wet state to a single-runner mill where the germ is separated and finally eluted. At a later stage milling is carried out in a modified high-speed hammer-mill into which water is fed continuously, the spray set up by the hammers keeping the screen clear.

The choice of a suitable milling procedure with heterogeneous material may simplify chemical separation at a later stage. This point is stressed

by H. E. Shiver[170] in a paper on the milling of cottonseed hulls. If the hulls are subjected to a superficial rubbing action, the pentosan content of the coarser product is 50% greater than in the ordinary grinding, and protein and fat are concentrated in the fine solution, whereas an intermediate lint product is clean enough for use in the cellulose industries. Large-scale experiments show that this can be effected in a Bauer attrition mill, the fibre being removed by air winnowing and recovered in a cyclone separator.

Measurement and control

E. U. Condon and E. C. Crittenden[171] have reported the proceedings of the 9th International Conference on Weights and Measures. With the growing need for more readily available and absolute standards, further research has been recommended into the use of spectral lines as a standard of length. The use of the triple point for water as an absolute point in defining a new standard scale of temperature has again been discussed but no decision taken.

Efficient methods of measurement of flow conditions when more than one phase is present have assumed new significance with the extending application of fluidization. J. M. Dotson, J. H. Holden, C. B. Seibert, H. P. Simons and L. D. Schmidt[172] suggest the use of specific inductive capacity as a measure of solids content in a gas stream ; no actual results are given, but the authors claim an accuracy of 1% in measurements on a fluid with 20% solids. The effect of moisture and other impurities is not discussed and only a very schematic diagram of the electrical system is given. Details of an instrument for measuring stack losses in fluidized-catalyst operation are given by J. H. Ranser and J. W. Hickey.[173] The intensity of light from a beam traversing the diameter of the stack is measured with a thermopile and recorded on an electrical recorder. A Pitot-tube, suitably modified to permit of air purging, measures the flow of gas and operates a ring-balance recorder. By Selsyn motor-coupling between the instruments, the concentration value is superposed on the ring-balance recorder pen to yield a self-integrating system showing total loss of catalyst.

In spite of the increased availability of radioactive materials[174] the extended application of this aid in process measurements is slow. S. D. Ross[175] draws attention to the Gagetron level indicator in a review of level measuring and control instruments. A patent[176] has been granted for an instrument based on the radioactive principle to indicate the position of the interface between immiscible liquids in an opaque container. Radiation from 0·2 mg. of radioactive material in a float is detected by a counter outside the container.

The control of fluid flow in high-pressure plant is considered in a paper[177] in which some of the features of the new coal-hydrogenation plant in the U.S.A. are described. Balanced mercury-ring gauges are said to be less sensistive than electrically actuated gauges for differential pressure measurement. In the Stratham gauge the differential pressure is made to expand one electrical conductor while another is compressed and these conductors form the arms of a Wheatstone bridge. A patent[178] has been granted for a simple form of this gauge where the flow orifice

is mounted directly on a flexible diaphragm which is used to modify the resistance of two wire grids embodied in an electrical bridge circuit. The main advantage of the electrical method is in its low inertia and it should be useful for measuring rapid variations in flow.

Air operation of control mechanisms is simply adapted to a wide range of operational conditions and remains more popular than electrical control. G. A. Philbrick[179] describes the variations which may be effected by air control mechanisms. 'On–off,' 'neutral zone' and 'proportional control' are described and 'reset' mentioned but not discussed in detail. R. H. Munch[180] stresses the need for clean, dry air in the satisfactory operation of pneumatic controllers, and describes some equipment for this purpose. Great interest is being shown by members of the paper trade on instrumental control. G. F. Akins[181] and G. K. Akins[182] describe controllers of use in the paper industry.

Control of fractionation column operation is discussed in some detail by G. W. Wilson[183] and I. D. M. Boyd.[184] Material balance and temperature control are considered and resistance and pressure-bulb instruments compared. A. J. Hornjeck[185] stresses the importance of response time in thermometer elements and compares a number of these from this point of view. Radiation losses from thermocouples in gas-temperature measurements are discussed by A. I. Dahl and E. F. Fiock,[186] who recommend the use of small rare-metal tubes pressed directly on to thermocouples used for temperature measurements on gas turbines. The authors also stress the errors which may arise by low speed of response. A. I. Dahl and P. D. Freeze[187] propose a simple method for measuring the temperature of rapidly rotating parts. The e.m.f. from the thermocouple is applied to the rotor coils of an electric motor driven by the rotating object. The e.m.f. generated in the stator coils is measured with an oscillograph. With minor alteration the device may be used to measure a number of temperatures. A patent[188] has been granted for an oscillographic method of flow measurement in which the speed of a freely suspended multi-bladed rotor in the gas stream is recorded by the impulses from a condenser plate situated near the periphery of the rotor.

J. J. Martin[189] points out that if suitable scales are chosen in calibrating rotameters the readings may be made to apply to all fluids by the application of a simple correction for density and viscosity. This is effected by recasting the normal rotameter equations so that the volume-rate of flow occurs in only one term of the equation. A patent rotameter[190] fitted with two floats gives direct readings of specific gravity and viscosity of flowing liquid.

F. D. Miles and D. Smith[191] give complete and practicable details of an autosiphon meter which is suitable for measuring highly corrosive fluids. Its accuracy is at least 1 in 500 even for an instrument capable of handling 280 tons per day.

Boiler-water treatment

Recent advances in the ion-exchange process are described by K. Kunin.[192] H. B. Gustafson[193] from an estimate of the consumption of zeolite in the U.S.A. in 1946 concludes that the ion-exchange process

can only account for a very small fraction of the water for boiler requirements, and he foresees no great expansion of its application. He draws attention to the fact that regeneration becomes progressively less complete and this greatly increases the cost of processing. G. Nonhebel[194] describes the results of 20 years use of zeolite-softened town water and process condensate in 300 and 800 lb./sq.in. boilers. Analysis of boiler water deposits are given and the results of routine boiler inspection.

A patent[195] has been granted for the use of processed coffee grains as a base-exchange resin for water softening. After treatment with a solution of sulphuric acid and other sulphates the coffee is roasted, soaked in sodium silicate and dried. A capacity of 10^4 grains calcium carbonate per cubic foot is claimed and regeneration is effected with 2% sodium chloride solution.

A major defect of the ion-exchange system is its inability to reduce the silica content of natural waters to a suitable concentration for boilers. W. B. Leaf[196] suggests a novel process for this purpose which involves the adsorption of silica on hydrated ferric oxide. Rusting cast iron chips produce a suitably colloidal oxide and pilot-plant tests show that the method is capable of dealing with water containing 200 parts per million of silica.

J. V. Robinson and W. W. Woods[197] have examined a number of antifoam agents mainly from the point of view of their interfacial tension in different media. They conclude that to be effective the antifoam agent must be insoluble in the foaming liquid and it reacts as an emulsion rather than as a film, as has been previously suggested. The theory of antifoam action is discussed by A. L. Jacoby[198] who carried out tests on a number of antifoaming materials. Octadecylamide shows no activity and castor oil and *n*-octadecyleruncamide only slight antifoaming qualities. High molecular weight diamides are effective and piperazine derivatives show increased foam-inhibiting properties with increase in length of substituent fatty acid chains. Patents[199,200] have been granted for the application of compounds of these types. It is clear from the recommendation of applying these in organic solvent that their solubility in water is low. The first patent also deals with the addition of 'depressants'—citric, tartaric and other acids—to prevent the adsorption of the foam-inhibitor on solid particles in the boiler water. Soluble silica-containing compounds are also deemed necessary and it is proposed to add these to the water if not already present.

A. A. Berk and J. Nigon[201] have examined a number of amines with reference to their use as additives to boiler water to inhibit corrosion in return condensate lines. For low-pressure boilers an amine which readily distils without decomposition is required and *cyclo*hexylamine satisfies the requirements. Above 60 lb./sq.in. this substance is less efficient than benzylamine and for the highest pressures morpholine has a suitable volatility. Where blow-down is very low the latter compound has the advantage of giving protection for long periods after its addition. When high blow-down rates are dictated by high total dissolved solids in the boiler, the life of the amine is of less importance and benzylamine is the most efficient of all the inhibitors.

R. C. Bardwell and J. J. Dwyer[202] review the various processes which

have been used to condition water for locomotive boilers. The lime–soda method is inexpensive and most widely applicable. Baryta softening is efficient but more expensive. Ion-exchange yields water with low dissolved solids but is conducive to oxygen pitting. The use of excess soda ash prevents scale formation but necessitates a rigorous blow-down schedule to remove precipitated sludge, and may yield strongly alkaline water giving rise to caustic embrittlement. The latter effect is specially dangerous in non-stationary boilers where mechanical stress may be superimposed on the normal pressure stress. Addition of sodium nitrate is effective in preventing intercrystalline corrosion and embrittlement. Castor oil and tannin foam-inhibitors have been almost universally replaced by polyamides and related compounds. The use of Diesel locomotives with light alloy cylinders and radiator parts necessitates water supplies which are low in dissolved solids and deaerated. Chromates are useful in preventing corrosion of light alloys in these conditions. D. D. Wright[203] recommends the use of chromate concentrations of 200 to 400 p.p.m. with p_H adjusted to 7·5–9·5 by caustic soda addition in engine cooling systems.

An apparatus is described by H. Rudy and K. R. Müller[204] for evaluating the scale-forming qualities of boiler water, and W. Wesley[205] has studied crystallographically the changes in solids deposited from boiler water before and after the addition of phosphates.

J. G. Sherrat[206] draws attention to the advantages in the use of the silica-assisted coagulating process suggested by Baylis for polluted surface water. Addition of a nearly neutralized solution of sodium silicate to alum-treated water containing suspended particles, gives an easily handled floc. Filter pore size can be increased, and the rate of settling is greater than with alum alone. The author records that in this way the capacity of one plant has been increased from 4·5 to approximately 7 million gallons per day and alum consumption is reduced. Silicate addition prevents after-precipitation in the clarified water, extends the p_H range in which clarification can be effected by alum and reduces the effect of low temperature on the rate of settling. No measurable increase in the silica content of the processed water is observed.

C. H. Carter[207] describes the apparatus and method used to clean 200 lb./sq.in. Stirling-type boilers with hydrochloric acid. The method is said to be more effective than mechanical cleaning and is certainly less laborious. The chief objection to acid cleaning of boilers is the danger of preferential attack at tube-plate junctions and this may be overcome by suitable inhibitors. A patent[208] has been granted for the use of a strongly alkaline mixture containing sodium and potassium hydroxides and phosphates for cleansing new boilers of oil and grease before use. H. E. Crossley[209] has examined the deposits on the exterior of boiler tubes and considers the conditions giving rise to deposition. He recommends the addition of magnesium oxide or other oxides in fine particulate form to reduce the dew point of gases with high sulphur trioxide content.

Ion-exchange

In a symposium on ion-exchange reported in *Industrial and Engineering Chemistry* the application of the process to problems other than water

demineralization is stressed. Production of dextrose from corn-starch by ion-exchange is being conducted in two pilot plants. T. H. Newkirk and M. Handelman[210] report results of tests carried out in a multi-stage exchange unit. The filtered liquor from steam hydrolysis of starch in presence of mineral acid, is freed from ash, acid, copper, iron and 5-hydroxymethylfurfuraldehyde by passage through a series of columns. Iron and copper are at first taken up by anion-exchangers in the early stages of the process but as these exchangers become exhausted the metals are displaced by other anions. The flow of liquor through the exchange bank can be altered so that it passes first through a nearly exhausted resin before contacting freshly regenerated material. Iron and copper displaced from the partially exhausted exchange are readsorbed in the succeeding unit so that some accumulation and recycling of these metals occurs. This is not found to be serious with respect to the final purity of the product. The main difficulty experienced is in regeneration, a steady decrease in capacity being noted as the process proceeds. Treatment at intervals with strongly acid and alkaline regenerants only partially restores activity. From experiments with a similar pilot plant for dextrose from corn-starch R. H. Rogge[211] finds many advantages over the older method of neutralization of the acid hydrolysis liquor with soda-ash followed with charcoal purification. Crystallized product yield has been increased from 82 to 90% and purity is improved. Sulphuric acid is used in the hydrolysis in place of the hydrochloric acid normally used. No mention is made by this author of difficulties in regeneration.

R. R. Legault, C. C. Nimmo, C. E. Hendel and G. K. Notter[212] show that ion-exchange may be made the basis of a simple process for the preparation of high-grade tartaric acid from winery still slops. An anion exchange in the chloride form is utilized and the tartaric acid is recovered by regeneration with sodium chloride solution. 3·6 lb. sodium chloride are required per pound of tartaric acid and the concentration is increased 15–18 times in the regenerated liquor. Some fouling of the exchange medium occurs due to sediment in the slop and this reduces the capacity. It is expected that filtration before the exchange stage will simplify regeneration and obviate the present process of caustic soda washing to remove the sediment.

Two valuable new exchange materials are described by R. Kunin and F. X. McGarvey.[213] These are Amberlite IRC–50, a weak-acid type cation exchanger, and IRA–400, a strongly basic anion resin. Both appear to be essentially monofunctional and the adsorption characteristics of the cation exchanger are sensitive to changes in p_H. Attention is drawn by R. Kunin and R. E. Barry[214] to the fact that the cation resin absorbs calcium ions in preference to sodium on the hydrogen cycle. Regeneration under these conditions is carried out with a strong mineral acid. The separation of some natural amino-acids and related compounds can be effected with the aid of these and other Amberlite resins. J. C. Winters and R. Kunin[215] show graphs of the absorption capacity of exchange resins with variation of p_H. With the aid of the two new resins it should be possible to conduct an almost quantitative separation of a mixture of lysine, histidine, leucine and glutamic acid. Unfortunately no data are given on the efficiency of regeneration, but unless

this is particularly adverse, it is comparatively unimportant in analytical and laboratory preparational work, and the new resins should be of great value in this field.

A new resin described by D. A. Robinson and G. F. Mills[216] is said to have covalent adsorption properties. The authors have examined the behaviour of the resin Duolite A-2 with a homologous series of carboxylic acids dissolved in acetone, water and in 'Shell solvent.' The curves obtained all follow a Freundlich law indicative of covalent attachment to the reactive group of the resin. There are few details of the nature of the material except that it is monofunctional with only amino-groups reactive, and retains a porous structure even when fully dehydrated.

G. A. Cruickshank and D. G. Braithwaite[217] draw attention to the fact that ion-exchange beds used in water purification may provide a culture ground for bacterial spores and discuss the sterilization of exchange resins. Cation resins with a phenol–formaldehyde base may be sterilized by washing with 0·25% formaldehyde solution without affecting the characteristics. All traces of formalin are removed during regeneration. A resin unattacked by formalin (Ionac A–300) is mentioned by H. Zowader,[218] who has used this resin to remove traces of formic acid from strong solutions of formaldehyde. The capacity and regeneration efficiency of the exchange medium is given and the cost of the process is estimated as 2·7 cents per pound of acid removed.

Materials

The relation of corrosion-resistance and method of fabrication is becoming more widely recognized. H. R. Clauser[219] stresses the need for co-ordination in the choice of materials, design and method of fabrication to ensure highest efficiency in operation. The design and manufacture of cast-iron chemical equipment is discussed by J. N. Bewsher.[220] Examples are given of good and bad features of design. This author emphasizes the well-known fact that only a limited number of foundries are capable of producing satisfactory cast iron vessels for chemical plant. G. C. Kiefer and C. H. Sheridan[221] have studied the effect of adverse heat treatment on the chemical and mechanical properties of stainless steels containing varying proportions of carbon, and re-state the desirability of maintaining less than 0·03% of this element in the alloy. More extensive tests by W. D. Binder, C. M. Brown and R. Fanks[222] on steels containing Cr 16–25, Ni 6–25, C 0·005–0·05 and N 0·002–0·15% show that nitrogen content also affects corrosion-rate near welds and this element should not be present in excess of 0·05%. The effect of molybdenum addition is also considered. Even in stainless steel stabilized against intergranular carbide formation during welding, corrosion may result from sigma-phase development near welds. This is stressed by A. C. Branch and J. L. Sweeten[223] in a paper on the fabricational limits in the choice of stainless steel for chemical plant. The special properties of a number of alloy steels are listed and the availability of rolled sections, plate, tubes, bars and castings discussed. Girder sections are available only in a very limited number of alloys and may have to be fabricated by bending and welding. Machining operations are discussed in considerable detail. In general machine operations are

only possible at about one-third of the rate attainable with ordinary steels and many operations can only be carried out in machines specially modified for use with stainless steels. In milling, twice the power is required and flame-cutting is best conducted with a special cutter which injects flux to dissolve the resistant oxides. The flux may result in contamination of the cut surface with subsequent loss of corrosion-resistance. In pressing and spinning frequent reheating or intermediate heat treatment is necessary as the metal has pronounced work-hardening qualities. Welding can be carried out with oxy-acetylene or by the normal electrical methods, and the argon-arc produces an excellent result on thin sheet. The general design of stainless steel plant is dealt with and the authors conclude with a cautionary note on constructing vessels with insufficient rigidity to withstand normal mechanical stresses such as may occur in the transport of the apparatus to the operating site.

Attention is drawn to the advantage in mechanical strength of clad steel in plant fabrication by W. G. Theisinger.[224] W. Barr and J. Erskine[225] describe a method of manufacturing stainless-clad steel. A continuous layer of steel is deposited by welding over the whole surface of a heavy slab of stainless steel and this is further built up by welding over it ½-in. thick steel plates edge-to-edge. On rolling this produces a stainless steel plate with a closely bonded mild-steel layer about 0·04 in. thick. When this is cut it may be rolled on mild steel so that bonding has only to be effected between the two mild steel surfaces. Bending and machining tests illustrate the efficiency of the bonding process and photomicrographs of welded sections show excellent homogeneity. Initial tests show that tubes can be similarly produced from composite billets to yield an effectively bonded lining of stainless steel. Clad steel plant is said to be less expensive than that constructed of stainless steel and with careful design should reduce machining difficulties.

C. F. Poe and E. M. van Vleet[226] have carried out tests on the resistance of an 18 : 8 stainless steel to a number of organic acids at room temperature and at 100° C. As the object was to find whether the steel was suitable for foodstuff handling it is surprising that the authors considered oxalic acid and that this was the only reactant which did attack the metal.

Materials research in the United States continues to progress towards the industrial production of metals either naturally rare or difficult to win from the ore. The physical and mechanical properties of tantalum are listed by G. L. Miller[227] and attention is drawn to its many uses. H. H. Uhlig and D. B. Broughton[228] mention some of the uses of titanium and zirconium, both of which are now available in usable quantities in America. The corrosion-resistance of these metals is the subject of a paper by E. A. Gee, L. B. Golden and W. E. Lusby.[229] Titanium is attacked by hydrochloric and sulphuric acids but is almost completely resistant to nitric acid at all concentrations. Zirconium is fairly resistant to all concentrations of hydrochloric, nitric and phosphoric acids but is attacked by concentrated sulphuric acid at elevated temperatures. The dangerous nature of zirconium oxide, to which the metal presumably owes its immunity from attack, may militate against its general use. At the moment the cost of zirconium is $200 per lb. while titanium can be produced for $5 per lb.

Glass equipment for pilot- and full-scale plant is steadily gaining favour in this country and is unsurpassed for general chemical resistance. J. W. Opie and W. J. Ward[230] discuss the advantages of glass in reactors of about 50-l. capacity. These can be arranged with robust stirrers, glands and fitments and the use of tilting cradles obviates the necessity for drain cocks and valves. Breakage costs are considered. Polythene compares favourably with glass and in certain cases is preferable for the storage of pharmaceutical products. It is available in the form of sheet, solid-drawn tubes up to 3-in. diam. and as bottles and carboys.[231] Larger-diameter tubes necessitate ribbon-winding and welding, for which a hot nitrogen jet is suggested. A major defect of polythene is its deformation at relatively low temperatures and it is not recommended for storage above 65° c. Its poor adherence to metal stressed by previous investigators is refuted by K. Stoeckhert.[232]

G. M. Kline,[233] in a materials review, mentions the uses of Teflon (polytetrafluoroethylene) and Kel–F (polymonochlorotrifluoroethylene). These materials, originally developed to handle fluorine compounds, are said to be essentially unattacked by all reagents other than molten alkali metals. Shaped by pressing at 300–305° c., they are transparent in thicknesses up to 0·25 in. and are machinable and capable of taking ordinary screw threads. Their non-adherent properties render them specially suitable for gland-packing and to this end they are being produced as spun fibre.

O. R. McIntire and R. N. Kennedy[234] have examined foamed polystyrene as a thermal insulating material. Its conductivity is decreased by reduction of bubble size, and infra-red radiation can be reduced by incorporating carbon black or aluminium powder in the plastic. A feature of this material for use in refrigeration is its impervious nature, which prevents water condensation within the lagging.

The nature and mode of formation of surface films has always been of interest to research workers on corrosion. Using a continuous-vacuum microbalance apparatus E. A. Gulbransen[235] has studied the effect of pre-treatment by degassing, hydrogen reduction and decarburization on oxide film formation. The author points out that no satisfactory physical reason has yet been produced for the parabolic law which appears to apply to the rate of iron oxidation. Auto-catalysis would appear to be a simple explanation of this. The temperature dependence of the reaction is related by an equation of the Arrhenius type. The reaction rate–temperature graph for molybdenum shows two distinct straight lines which indicate the very unusual phenomenon of higher activation energy at the more elevated temperature. No explanation is suggested.

F. W. H. Matthews[236] describes a new 'beaker-corrosion test' for bearing metals in oil. Attack is only noticeable in presence of metallic copper which appears to be a catalyst. The copper is inactivated rapidly, and consistent results are only obtained if the copper is removed and cleaned at two-hourly intervals during the test. Polar-type rust-inhibitors for oils are believed by H. R. Baker and W. A. Zisman[237] to depend on the hydrogen bonding of hydrophilic groups in the substance with the metal surface. Ideally the parent molecule of the inhibitor should be a high molecular weight homologue of the oil and be only slightly soluble in it.

H. R. Baker, D. T. Jones and W. A. Zisman[238] emphasize the fact that different corrosion tests may have a considerable effect on the result. In testing polar-type rust-inhibitors, spray and fog tests have a much higher leaching action than the A.S.T.M. turbine oil rusting test, in which the metal sample is in contact with a mechanically-stirred mixture of oil and water. They compare these methods with a static water-drop procedure which is claimed to be more discriminating. An inhibitor (V.I.P.)[239] for the protection of packaged metallic objects against atmospherical corrosion is a white crystalline stable product which slightly sublimes at room temperature. In an enclosed space this deposits a protective film on the stored article. It is said to be odourless, non-toxic and non-irritant. D. Wyllie and G. C. N. Cheesman,[240] from measurements on the progressive change in concentration of sodium nitrite as a corrosion-inhibitor for steel in sea-water, conclude that its action may be catalytic. In presence of sodium nitrate a thin semi-protective film forms; increasing the concentration leads to destruction of the film and local pitting. In a later paper[241] the authors recommend the addition of traces of sodium hexametaphosphate and sodium carbonate to obviate this defect.

The results of an extensive series of experiments on the cathodic protection of oil pipelines in Syria are reported by W. C. R. Whalley.[242] A number of methods were applied in protecting various sections of some hundreds of miles of pipe. Copper–copper sulphate electrodes gave local protection but a very large number would have been necessary to ensure protection of the whole line. Magnesium and zinc used as sacrificial anodes were found to be affected by weather conditions to some extent and all self-generating methods gave potentials too low for distribution over long lengths of the pipe. The most economical and effective method was found to be the provision of d.c. generators at suitable intervals along the pipeline. The pipe was covered with a multilayer pitch and rubber-coating, and application of a potential of 3 v. at each generating point gave complete protection without hydrogen evolution.

K. R. Butlin and W. H. J. Vernon[243] describe the events which led to the discovery and isolation of the bacteria involved in the attack of steel and cast-iron pipes in clay soils, and go on to discuss conditions in which corrosion is most severe. With the collaboration of a number of District Councils a wide survey has been effected and this shows that although clay soils are generally conducive to the growth of *Desulphovibrio desulphuricans*, no attack occurs in clays with low sulphate content. Methods of laboratory culture have been developed and it has been shown that normal antiseptics such as chlorine and phenol are ineffective in inhibiting the growth of the organism. Potassium tellurite, cetyl pyridinium bromide, *o*-nitrophenol and potassium dichromate show promise as inhibitors but there are indications that these are less effective in presence of ferrous ions. In field tests a number of protective coatings for pipes have been examined. The ordinary bituminous hessian wrapping gives no protection although $\frac{3}{8}$-in. bituminous coating is satisfactory; concrete coating or packing in gravel is advantageous. Experiments are being carried out on cathodic protection by the use of sacrificial anodes.

J. A. Hutcheson[244] draws attention to the problems in the selection of materials of construction for atomic energy generating piles. Unusual corrosion problems are experienced and exceedingly high purity is required in parts subjected to neutron bombardment. Special modes of fabrication are required to prevent any leakage of radioactive material.

Plant design and process development

The extending application of complex chemotherapeutics is reflected in development of industrial processes for their preparation on a large scale. Special problems in the chemical engineering field are the necessity for very high standards of purity and unusual flexibility of plant operation. T. R. Olive[245] describes plants producing streptomycin by the biological method and chloromycetin by a multistage chemical process. In the biological unit the plant has had to be designed with a view not only to freedom of contamination and ease of cleaning but also to sterilization.

J. A. Lee[246] gives a general description of a new plant in the U.S.A. for the manufacture of anhydrous hydrocyanic acid by direct reaction of methane, air and ammonia on a platinum catalyst. A flowsheet and photographs are presented but no details of yield or operating conditions. The product is converted directly to acetone cyanhydrin in a continuous process. Instrumentation is very complete and the plant is almost fully automatic, the raw materials being proportioned mechanically so that danger of explosion is minimized under all conditions. Failure of essential parts of the plant lead to the operation of an automatic and controlled shut-down procedure.

R. W. Rutherford and K. Ruschin[247] discuss details of a new 50,000 tons/annum ammonium sulphate plant nearing completion in Southern India. Wood is converted to charcoal which is used for producer gas manufacture, and hydrogen is obtained by the steam–iron oxide reaction. The producer gas is used to reduce the iron oxide, the waste gas being oxidized completely with air and scrubbed with ethanolamine to yield nitrogen for the ammonia-synthesis gas. Carbon dioxide recovered in the ethanolamine regeneration is used in the gypsum process for ammonium sulphate manufacture. 12 ft.-diam. producers are used and operation is satisfactory in spite of the low ash content of the fuel. Sulphur in the producer gas is low and is removed by scrubbing with a solution of soda-ash. Traces of carbon monoxide and dioxide are removed at the second-last stage of compression with copper–ammonium formate and caustic soda. Complete flowsheets of the process are given.

Attention is drawn by M. L. Kastens, J. F. Dudley and J. Troeltzsch[248] to the great increase in synthetic methanol output over the past few years in the United States. In 1947 only 80 million gal. were produced as opposed to 1 million in 1927 and plant is in course of erection to increase this almost threefold. Disused ammonia-synthesis plant has been adapted for this purpose in a number of cases. Operating conditions for modern plant are 1000 atm. and 400° c. and at least one plant uses carbon dioxide in addition to the monoxide in the synthesis.

The preparation of unsaturated higher alcohols by sodium reduction of olefines on a plant scale is the subject of a paper by M. L. Kastens

and H. Peddicord.[249] An interesting feature of the paper is the description of the method of handling sodium which is delivered in 10-ton tank waggons and utilized in 2000-lb. batch reaction charges.

Most modern caustic soda plant in American operates on the electrolytic process. Low electrical power costs, increased value of chlorine and its compounds, and ease of control and operation are responsible for the new trend.[250] Diaphragm- rather than mercury cells are employed in the latest units. Notes on the transport and storage of liquid chlorine are given by J. V. Hightower[251] and the thermodynamic properties of chlorine are discussed by R. E. Hulme and A. B. Tillman.[252]

S. B. Cormack and L. Stubbs[253] give details of an interesting modification in chamber plant which enables 96% acid to be manufactured. One Glover only is used for denitration of the Gay-Lussac acid, the other being utilized for concentrating chamber acid. The concentrating tower is similar to the Glover tower but constructed and packed with more resistant materials and is carefully lagged. Burner gases enter the towers (in parallel) at 800° c. and leave at 250° c. The concentrated acid leaves the tower at 250–280° c.; approximately half the SO_3 can be converted to 96% acid. The process has been in use for some years and no special difficulties are reported.

Some novel features are embodied in the new high-pressure experimental coal-hydrogenation plant nearing completion for the United States Bureau of Mines. Details are presented by M. L. Kastens, L. L. Hirst and C. C. Chaffee.[254] The plant operates at 10,300 lb./sq.in. and internally lagged carbon-steel vessels are used in the converters and preheaters. In future plant spiral-wound vessels will be tried. The coal–oil slurry (46% solid) has a viscosity of about 5000 cp. at 210° F. and helical screw pumps are employed for low-pressure pumping with ram displacement pumps for high-pressure injection. The design is conventional except that special standards have had to be adopted for this operating pressure. The use of lens-rings, common in British and German plant, appears to be novel in the U.S.A. An attempt will be made to manufacture petroleum in two stages in place of the four stages employed in German units, and higher thermal economy is expected. S. Weller, M. G. Pelipetz, M. Kuhn, S. Friedman and E. L. Clark[255] have experimented with the use of coke-oven gas in place of hydrogen for coal-hydrogenation. The efficiency is much lower and increasing the temperature above 450° c. results in high gasification and a lower yield of liquid products. It is interesting to note that the analysis in these experiments was carried out by mass spectrometer. R. R. Maccary and R. F. Fey[256] discuss the application of various standard formulae in the design of thick-walled pressure vessels. The advantages of pre-stressed vessels are considered. Autofrettage is rendered difficult by the complex behaviour of thick-walled vessels even under carefully controlled stress and the ribbon-wound vessels favoured by German chemical engineers can be constructed with almost ideal internal stress characteristics. The simple Lamé formula may be applied to the individual layers. The main defect of wound vessels is the difficulty of satisfactorily fitting end closures and a number of methods are described by the authors.

Miscellaneous

The need for more accurate physical data on organic compounds promotes mathematical conjecture rather than experimental physical chemistry, and a growing number of papers appears each year on the prediction of thermodynamic properties. R. R. Dreisbach and R. S. Spencer[257] suggest methods of extrapolating vapour pressure data and B. W. Gamson[258] proposes the evaluation of 'reduced thermal conductivity' of gas by the usual reduced temperature and pressure relationships. H. P. Meissner[259] draws attention to the uses of the parachor in evaluating critical constants. J. Joffe[260] compares thermodynamic data from pseudo-critical derivation with that obtained by the kinetic theory. He concludes that in general the former method yields results more useful for the chemical engineer but care must be exercised in applying the method to mixtures where molecular interaction may occur. R. R. Wenner[261] summarizes knowledge of the relations of free energy and reaction equilibrium. Large errors may be introduced from uncertain values of entropy and total heats. The author illustrates the application of free energy principles in a variety of reactions. The prediction by this method that the ease of hydration of olefines increases with decrease in number of carbon atoms appears to be contrary to the experimental findings. R. H. Wilhelm[262] points out that information on rates of reaction are particularly scarce. The Arrhenius equation has valuable properties for prediction of reaction kinetics but the constants are known accurately in only a very few cases, and no complete series can be constructed. In a similar way equations relating to heterogeneous catalysis reactions are well established but the constants are seldom available. It is clear that most predictional methods can only be regarded as approximate until the validity of reference points is established by experiment.

P. Guillaumeron[263] gives an account of a plant for the manufacture of hydrogen from coke-oven gas. Complication arises in the many impurities present and reference is made to the azeotropes of acetylene with ethane and ethylene as an example. To produce a gas with less than 2% of carbon monoxide the product gas is scrubbed with liquid nitrogen. This results in hydrogen containing 10 p.p.m. carbon monoxide and 10% nitrogen and the gas is suitable for ammonia synthesis purposes.

The use of mixed refrigerants for process refrigeration is recommended by F. Carr.[264] The authors points out that this yields greater flexibility of operation with smaller irreversible losses at the expansion valve and mentions ethane–propane–butane as a mixture with a wide operating range.

A number of articles on pilot plant have appeared in American literature during the past year. C. O. Brown[265] makes a distinction between 'research data' and results from pilot-plant measurements of power requirements, pressure drops, film coefficients and similar information directly related to the full-scale project. G. T. Gwin and L. T. Yule[266] propose 'standardized' pilot plant and proceed to give line sketches of a large number of plant units which presumably would be held in stock in much the same way as glass laboratory equipment. J. A. Ridgway[267] makes a similar suggestion but illustrates his article with detailed drawings

of useful gadgets rather than general plant. It is not clear how the varying requirements of pressure, volume and other important variables are to be dealt with unless all plant is designed for the maximum possible requirements. A vast number of heat exchangers, pumps and instruments will be necessary to deal with fluids with physical constants such as the viscosity varying 500-fold. A further note of caution which might be struck is that chemical plant as opposed to laboratory glassware deteriorates more rapidly in storage than in use. The more usual approach to pilot problems is that by R. G. Heitz, C. F. Oldershaw, W. E. Brown and R. D. Barnard,[268] who describes the plant used to produce 99% ethane from natural gas originally containing 2·8%. The absorption of carbon dioxide in this process must be virtually complete and a special column was designed for this purpose. On the other hand, a 3000 lb./sq.in. heat exchanger was constructed from a salvaged bomb. Non-critical liquid levels were measured by a pet-cock system while a special hot-wire level instrument was constructed for more accurate measurements. These authors give details for a simple methane refrigerator for laboratory use. Difficulties in converting a process from laboratory- to plant-scale are enumerated by L. W. J. Loveless[269] with reference to a process for making acetic anhydride by non-catalytic thermal dehydration.

Safety

In a symposium in *Industrial and Engineering Chemistry*[270] the design of American radio-chemical laboratories to obviate danger to workers and local inhabitants is discussed and illustrated. Ion-exchange is used to recover radioactive substances from dilute liquid effluents, the exchange medium being ashed to concentrate the product. This method is preferable to the disposal of radioactive wastes at great dilution in streams or rivers, reports W. A. Rodgers,[271] as certain active materials may be concentrated by algae or other forms of aquatic life. British radiochemical laboratories[272] differ in many details from their American counterpart. At the British Radioactive Centre where large quantities of radium are stored and radioactive barium carbonate, acetic acid and ^{14}C are prepared, special emphasis is laid on efficient venting of working areas, as personal contamination most commonly occurs from gaseous reactants.

In the official Report on Alkali Works (*loc. cit.*)[113] attention is drawn to a case where blockage of a vapour main on sulphate of ammonia plant resulted in accumulation of gas which caused the death of a workman in a manhole 50 yards away.

E. M. Harris[273] draws attention again to the dangers associated with the use of perchloric acid. Contamination with organic material is the most common cause of explosion but the anhydrous acid is itself unstable and may detonate. Although the Los Angeles explosion in which 15 persons were killed and 400 injured was initiated in a tank containing perchloric acid and acetic anhydride, this mixture is still regarded as dangerous only when 'organic material' is present as a contaminant. It may be overlooked that acetic anhydride is both organic and dehydrating and with perchloric acid represents an explosive mixture irrespective of any further additives.

References

[1] *Proc. nat. Acad. Sci., Wash.*, 1948, **34**, 530
[2] *Chem. Engng.*, 1949, **56** (5), 96
[3] *C. R. Acad. Sci., Paris*, 1948, **227**, 892
[4] *Chem. Engng. Progr.*, 1948, **44**, 537
[5] Ibid., 1949, **45**, 39
[6] *Chem. Engng.*, 1949, **56** (5), 104
[7] Ibid., 130
[8] *Chem. Engng. News*, 1948, **26**, 2006
[9] B.P. 605,361
[10] B.P. 609,982
[11] *Chem. Engng.*, 1949 **56** (5), 128
[12] *Chem. & Ind.*, 1949, 87
[13] Ibid., 88
[14] *Chem. Engng.*, 1948, **55** (9), 114 and 248
[15] *Ind. Eng. Chem.*, 1949, **41**, 1099
[16] Ibid., 1104
[17] Ibid., 1117
[18] Ibid., 1206
[19] Ibid., 1161
[20] Ibid., 1099
[21] Ibid., 1191
[22] Ibid., 1174
[23] Ibid., 1184
[24] Ibid., 1148
[25] Ibid., 1135
[26] Ibid., 1124
[27] Ibid., 1213
[28] Ibid., 1227
[29] Ibid., 1238
[30] *Chem. Engng. Progr.*, 1948, **44**, 707
[31] Ibid., 1949, **45**, 563
[32] *Chem. Engng.*, 1949, **56** (5), 112
[33] *Coke and Gas*, 1949, **11**, 64
[34] *Chem. Engng.*, 1949, **56** (5), 115
[35] *Chem. Engng. Progr.*, 1949, **45**, 102
[36] *Chem. Engng.*, 1948, **55** (12), 124
[37] B.P. 623,264
[38] *Proc. Inst. chem. Engrs., Preprint*
[39] *Trans. Amer. Soc. mech. Engrs.*, 1948, **70**, 689
[40] *Ind. Eng. Chem.*, 1949, **41**, 1789
[41] *Proc. chem. Engng. Grp., Preprint*
[42] *Ind. Eng. Chem.*, 1949, **41**, 2209
[43] *Trans. Inst. chem. Eng., Preprint*
[44] Ibid.
[45] Ibid.
[46] *Chem. Engng. Progr.*, 1949, **45**, 51 and 129
[47] *Ind. Eng. Chem.*, 1949, **41**, 1945
[48] *Proc. roy. Soc.*, 1948 [A], **194**, 147
[49] *Trans. Amer. Soc. mech. Engrs.*, 1949, **71**, 259
[50] *Engineering*, 1949, **167**, 21
[51] *Angew. Chem.*, 1948, **20B**, 289
[52] *Gesundsheitsing*, 1948, **69**, 122
[53] *Chem.-Ing. Tech.*, 1949, **21**, 95
[54] *Trans. Inst. mar. Engrs.*, 1948, **60** (11), 223
[55] *Internat. Chem. Eng.*, 1949, **30**, 354
[56] *Gas-u. Wasserfach*, 1949, **90**, 263
[57] *Heat. Pip. Air Condit.*, 1948, **20** (3), 121
[58] *Bottler and Packer*, 1949, **23** (1), 17
[59] *J. Inst. Fuel*, 1949, **22**, 209
[60] *Combustion*, 1948, **20** (9), 39
[61] B.P. 603,829

[62] B.P. 617,871
[63] *Chem. Engng.*, 1948, **55** (12), 119
[64] *Ind. Eng. Chem.*, 1949, **41**, 1037 and 1048
[65] Ibid., 1070
[66] Ibid., 1948, **40**, 2118
[67] Ibid., 1949, **41**, 78
[68] *Chem. Engng. Progr.*, 1949, **45**, 342
[69] *Chem.-Ing. Tech.*, 1949, **21**, 293
[70] *Petrol. Refin.*, 1949, **28** (1), 106
[71] *Ind. Eng. Chem.*, 1949, **41**, 1277
[72] *J. Soc. chem. Ind.*, 1949, **68**, 88, 119 and 299
[73] *Trans. Faraday Soc.*, 1948, **44**, 629 and 636
[74] *J. Soc. chem. Ind.*, 1949, **68**, 131
[75] *J. chem. Soc.*, **1949**, 1054
[76] *J. Soc. chem. Ind.*, 1940, **68**, 26
[77] *Ind. Chemist*, 1949, **25**, 238
[78] *Chem. Engng. Progr.*, 1949, **45**, 359
[79] *Ind. Eng. Chem.*, 1949, **41**, 1953
[80] Ibid., 1056
[81] *Chem. Engng. Progr.*, 1949, **45**, 435
[82] *Petrol. Refin.*, 1948, **27**, 119
[83] *Chem. Engng. News*, 1948, **27**, 910
[84] *Ind. Eng. Chem.*, 1949, **41**, 331
[85] *Chem. Engng. Progr.*, 1949, **45**, 553
[86] *Ind. Eng. Chem.*, 1949, **41**, 1357
[87] *Chem. Engng. Progr.*, 1949, **45**, 323
[88] Ibid., 218
[89] Ibid., 241
[90] Ibid., 253
[91] *Trans. Inst. chem. Engrs., Preprint*
[92] *Chem. Engng. Progr.*, 1949, **45**, 188
[93] *Ind. Eng. Chem.*, 1949, **41**, 1366 and 1369
[94] *Chem. Engng. Prog.*, 1948, **44**, 681 and 771
[95] Ibid., 1949, **45**, 65
[96] *Ind. Eng. Chem.*, 1949, **41**, 2298 and 2303
[97] *J. Inst. Petrol.*, 1949, **35**, 73
[98] *Ind. Eng. Chem.*, 1949, **41**, 218
[99] Ibid., 2224
[100] *Industr. Chem. chem. Mfr.*, 1949, **25**, 5
[101] U.S.P. 2,435,115
[102] B.P. 617,860
[103] B.P. 601,921
[104] *Industr. Chem. chem. Mfr.*, 1949, **25**, 31
[105] *Chem. Engng.*, 1949, **56** (9), 112
[106] *Ind. Eng. Chem.*, 1949, **41**, 65
[107] Ibid., 566
[108] B.P. 618,196
[109] B.P. 610,412
[110] *Iron Coal Tr. Rev.*, 1949, **158**, 292
[111] *Heat. Vent.*, 1948, **40** (7), 80
[112] *Proc. chem. Eng. Grp., Preprint*
[113] 85th Report on Alkali Works, H.M.S.O., 1949
[114] *U.S. Bur. Min. Rep. Invest.*, 1948, 4278
[115] B.P. 613,915
[116] *Angew. Chem.*, 1948, **20B**, 335
[117] *Ind. Eng. Chem.*, 1949, **41**, 38
[118] B.P. 613,883
[119] *Proc. Inst. chem. Engrs., Preprint*
[120] *Chem. Engng. Progr.*, 1949, **45**, 539
[121] Ibid., 25
[122] *Ind. Eng. Chem.*, 1949, **41**, 754
[123] B.P. 612,592

[124] U.S.P. 2,390,212
[125] *Paper Tr. J.*, 1948, **127** (25), 26
[126] *Angew. Chem.*, 1948, **20B**, 235
[127] B.P. 602,818 and 602,861
[128] *Industr. Chem. chem. Mfr.*, 1949, **25**, 391
[129] B.P. 617,877
[130] B.P. 610,036 and 610,047
[131] *Chem. Engng.*, 1949, **56** (9), 92
[132] B.P. 617,776
[133] *Z. Ver. dtsch. Ing.*, 1948, **90**, 347
[134] *Chem. Engng.*, 1949, **56** (4), 98
[135] B.P. 616,032
[136] *Industr. Chem. chem. Mfr.*, 1949, **25**, 81
[137] *Ind. Eng. Chem.*, 1949, **41**, 22
[138] *Industr. Chem. chem. Mfr.*, 1949, **25**, 401
[139] *Ind. Eng. Chem.*, 1948, **40**, 1708
[140] *Chem. Engng. Progr.*, 1949, **45**, 545
[141] *Ind. Eng. Chem.*, 1949, **41**, 973
[142] *Nature*, 1948, **162**, 224
[143] *Chem. Engng.*, 1948, **55** (12), 117
[144] B.P. 605,149
[145] B.P. 604,770
[146] B.P. 612,011
[147] B.P. 610,832
[148] *Ind. Eng. Chem.*, 1949, **41**, 61
[149] *Chem. Engng. Progr.*, 1949, **45**, 482
[150] Ibid., 573
[151] *Chem. Weekbl.*, 1949, **45**, 325
[152] Ibid., 290
[153] *J. Soc. chem. Ind.*, 1949, **68**, 59
[154] Ibid., 91
[155] *J. sci. indust. Res., India*, 1948, **7A**, 484 and 487
[156] *J. Soc. chem. Ind.*, 1948, **67**, 289
[157] *Trans. Inst. chem. Engrs., Preprint*
[158] *Chem. Engng. Progr.*, 1949, **45**, 477
[159] *Industr. Chem. chem. Mfr.*, 1949, **25**, 362
[160] *Chem. Engng. Progr.*, 1949, **45**, 81
[161] B.P. 620,845
[162] *Trans. Inst. chem. Engrs., Preprint*
[163] *Ind. Eng. Chem.*, 1949, **41**, 1686
[164] *Trans. Inst. chem. Engrs., Preprint*
[165] *Ind. Eng. Chem.*, 1948, **40**, 2289
[166] *Chem. Engng. Progr.*, 1949, **45**, 508
[167] *J. Soc. chem. Ind.*, 1949, **68**, 80
[168] Ibid., 138
[169] *Chem. Engng.*, 1949, **56** (6), 92
[170] *Ind. Eng. Chem.*, 1949, **41**, 978
[171] *Chem. Engng. News*, 1949, **27**, 982
[172] *Chem. Engng.*, 1949, **56** (10), 129
[173] *Ind. Eng. Chem.*, 1949, **41**, 1244
[174] *Chem. Engng. News*, 1948, **26**, 2260
[175] *Chem. & Ind.*, 1948, 924
[176] B.P. 602,179
[177] *Chem. Engng.*, 1949, **56** (8), 107
[178] B.P. 613,478
[179] *Chem. Engng. Progr.*, 1948, **44**, 675
[180] *Ind. Eng. Chem.*, 1949, **41**, 97A.
[181] *Paper Ind. and World*, 1949, **30**, 1618
[182] Ibid., 1748
[183] *Oil Gas J.*, 1948, **47**, 63
[184] *Petrol. Refin.*, 1948, **27**, 115 and 594
[185] *Trans. Amer. Soc. mech. Engrs.*, 1949, **71**, 121

[186] Ibid., 153
[187] *J. Res. nat. Bur. Stand.*, 1948, **41**, 601
[188] B.P. 606,278
[189] *Chem. Engng. Progr.*, 1949, **45**, 338
[190] U.S.P. 2,437,247
[191] *J. Soc. chem. Ind.*, 1949, **68**, 133
[192] *Ind. Eng. Chem.*, 1949, **41**, 55
[193] Ibid., 464
[194] *J. Inst. Fuel*, 1949, **22**, 140 and 156
[195] U.S.P. 2,391,951
[196] *J. Amer. Wat. Wks Ass.*, 1948, **40**, 980
[197] *J. Soc. chem. Ind.*, 1948, **67**, 361
[198] *J. phys. colloid Chem.*, 1948, **52**, 689
[199] B.P. 602,726
[200] U.S.P. 2,428,775
[201] *U.S. Bur. Min. Tech. Paper* 714
[202] *Ind. Eng. Chem.*, 1948, **40**, 1376
[203] *Canad. Chem.*, 1948, **32**, 533
[204] *Chem.Ing.Tech.*, 1949, **21**, 106
[205] Ibid., 63
[206] *J. Soc. chem. Ind.*, 1949, **68**, 158
[207] *Pulp Pap. Ind.*, 1948, **22** (12), 86
[208] U.S.P. 2,439,784
[209] *Trans. Inst. chem. Engrs., Preprint*
[210] *Ind. Eng. Chem.*, 1949, **41**, 452
[211] Ibid., 2070
[212] Ibid., 466
[213] Ibid., 1265
[214] Ibid., 1269
[215] Ibid., 460
[216] Ibid., 2221
[217] Ibid., 472
[218] *Chem. Engng. Progr.*, 1949, **45**, 279
[219] *Mater. & Meth.*, 1949, **29** (3), 70
[220] *Industr. Chem. chem. Mfr.*, 1949, **25**, 219 and 262
[221] *Amer. Iron and Steel Inst. Yr. Bank.*, 1948, 476
[222] *Trans. Amer. Soc. Mat.*, 1949, **41**, 1301
[223] *Trans. Inst. chem. Engrs., Preprint*
[224] *Oil Gas J.*, 1948, **46**, 275
[225] *Proc. chem. Engng. Grp., Preprint*
[226] *Ind. Eng. Chem.*, 1949, **41**, 208
[227] *Industr. Chem. chem. Mfr.*, 1949, **25**, 388
[228] *Ind. Eng. Chem.*, 1949, **41**, 2153
[229] Ibid., 1668
[230] *Chem. & Ind.*, 1948, 782
[231] *Industr. Chem. chem. Mfr.*, 1949, **25**, 25
[232] *Chem.-Ing.-Tech.*, 1949, **21**, 146
[233] *Ind. Eng. Chem.*, 1949, **41**, 2132
[234] *Chem. Engng. Progr.*, 1948, **44**, 727
[235] *Ind. Eng. Chem.*, 1949, **41**, 1385
[236] *J. Inst. Petrol.*, 1949, **35**, 436
[237] *Ind. Eng. Chem.*, 1948, **40**, 2338
[238] Ibid., 1949, **41**, 137
[239] *Chem. Age*, 1949, **60**, 725
[240] *J. Soc. chem. Ind.*, 1949, **68**, 165
[241] Ibid., 209
[242] *J. Inst. Petrol.*, 1949, **35**, 705
[243] *Proc. chem. Engng. Grp., Preprint*
[244] *Min. and Metall.*, 1948, **29**, 484
[245] *Chem. Engng.*, 1949, **56** (10), 107
[246] Ibid., **56** (2), 134
[247] *Trans. Inst. chem. Engrs., Preprint*

[248] *Ind. Eng. Chem.*, 1948, **40**, 2231
[249] Ibid., 1949, **41**, 438
[250] *Chem. Engng.*, 1948, **55** (12), 112
[251] Ibid., 1949, **56** (1), 96
[252] Ibid., 99
[253] *J. Soc. chem. Ind.*, 1949, **68**, 162
[254] *Ind. Eng. Chem.*, 1949, **41**, 870
[255] Ibid., 972
[256] *Chem. Engng.*, 1949, **56** (8), 124; **56** (9), 105; and **56** (10), 120
[257] *Ind. Eng. Chem.*, 1949, **41**, 1363
[258] *Chem. Engng. Progr.*, 1949, **45**, 154
[259] Ibid., 149
[260] Ibid., 160
[261] Ibid., 194
[262] Ibid., 208
[263] *Chem. Engng.*, 1949, **56** (7), 105
[264] *Ind. Eng. Chem.*, 1949, **41**, 776
[265] Ibid., 1948, **40** (7), 63A
[266] Ibid., 1949, **41**, 862
[267] Ibid., 1082
[268] Ibid., 1540
[269] *Industr. Chem. chem. Mfr.*, 1949, **25**, 325
[270] *Ind. Eng. Chem.*, 1949, **41**, 227
[271] *Chem. Engng.*, 1949, **56** (2), 118
[272] *Industr. Chem. chem. Mfr.*, 1949, **25**, 316
[273] *Chem. Engng.*, 1949, **56** (1), 116

WATER

By ROY C. HOATHER, B.Sc., Ph.D., F.R.I.C.

AN event of outstanding interest in relation to water supply during the year was the First Congress of the International Water Supply Association, which was held at Amsterdam in September. Representatives of about 24 countries were present at the Congress. Among the technical subjects discussed were 'Disinfection of water mains after laying and carrying out repairs' and 'Standards for the expression of results of the physical, chemical and bacteriological examination of drinking water.' The Proceedings are to be published in 1950.

Coagulation

The programme of the Congress mentioned above included a visit to Rotterdam waterworks, where a pilot plant on the sludge-blanket principle was seen in operation. The coagulant on this plant was ferric iron, the metal being obtained in solution by passing the water between steel plates carrying a suitable potential, and oxidized by chlorine.

The recent development in coagulation attracting most interest at present is the use of 'activated' sodium silicate. Sherratt[1] describes the operation of this process in two large works, purifying grossly polluted rivers waters for industrial uses. The material used is commercial sodium silicate which has to be diluted to a concentration of 5·3% and then neutralized with sulphuric acid until its alkalinity is 1000 to 1350 p.p.m. After a period of 'ageing' which, with dilution water containing only low concentrations of mineral salts, is usually about 2 hours, the silicate is then diluted again four times, after which it is stable as a sol for a minimum time of about 24 hours, during which it must be used.

The silicate is added to the water either with, or about 2 minutes before, the dose of aluminium sulphate also used. The ratio of silica to aluminium sulphate used at these plants is approximately 1 to 4. In drought conditions with one of the highly polluted raw waters (River Mersey) the necessary dose of aluminium sulphate may be as much as 140 p.p.m., but clarification is often unobtainable with any practicable dose, without the silica. In general it is claimed that the improvement in coagulation and reduction in settlement time due to the use of silica is so great that substantial economy may be made in capital expenditure on the treatment plant.

Henry[2] discusses the neutralization of silica by scrubbed 10% carbon dioxide produced by burning fuel oil, and the application of the silica sol thus produced as a coagulant in softening with lime. Curves are given for the activity and stability of the sols prepared over a range of percentage neutralization. The data thus obtained indicate that 1·5% silica sols should generally be neutralized to the extent of about 50%, which can, however, be varied according to the conditions of use.

Langelier and Ludwig[3] have given extensive experimental data, with theoretical interpretation, on the mechanism of flocculation of suspensions

prepared from typical American soils. They show that a very important factor in chemical coagulation is the variation in the cation-exchange capacity of the turbidity particles from different soils. Because of the many variables involved, they find that flocculation phenomena cannot be formulated in simple mathematical terms, but may nevertheless be explained through the exchange and hydrolysis reactions which appear to be the two basic factors.

Softening

The report of the Water Softening Sub-Committee of the Central Advisory Water Committee appointed by the Minister of Health has been published recently.[4] The terms of reference of the Sub-Committee were :

'Whether it is desirable, and if so, feasible, that public water supplies should be softened in areas where there is a high degree of hardness; the effect of softening on the finances of water undertakings and the resultant cost to consumers, as compared with economies in other directions; the degree of hardness to which water softening is desirable, and the effect on trade and industrial undertakings if softened water is supplied.'

Their report includes a very considerable amount of data, and covers the subject thoroughly, especially from the aspect of the domestic consumer, whose interests are expressed as far as possible in quantitative terms. They consider that the soap-precipitating power of a water of hardness 200 p.p.m. may reasonably be taken as 0·25 oz. per gal., and they calculate that the wastage of soap in personal and domestic washing, due to this hardness, amounts to approximately 9 lb. per head per annum. This figure, however, represents what the wastage is when soap is freely available rather than the wastage under conditions which encourage the use of unrationed products.

The Sub-Committee conclude that :

'1. Undertakers already softening their water supplies are doing a service to the community which is well worth the cost. They should continue to operate their plants (subject to the availability of materials) to produce as soft a water as possible consistent with other technical requirements.

'2. Undertakers supplying hard water and so situated as to carry out softening at reasonable cost should be encouraged to plan to do so as soon as labour and materials can be spared from more urgent matters, but should reserve their final decision on softening until the last possible moment so as to be able to take into consideration the latest developments.

'3. Undertakers unable for any reason to see their way to providing soft water for some time to come should, nevertheless, keep in mind the desirability of doing so and should, so far as possible, plan accordingly, not, however, making a final decision until it is possible to implement it.'

The possibility of the use of synthetic detergents continuing to expand at the expense of the use of soap is a consideration which is discussed by

the Sub-Committee, but they find it impossible to assess the position a few years hence, as the whole subject is in a state of rapid development.

On the whole, and with certain reservations, the report represents a marked advance of recognized opinion in favour of the softening of their supplies, by water undertakings, to lower figures than have been customary. For example, one of the suggestions is that:

> 'All undertakers supplying water between 100 and 200 p.p.m. hardness should be informed of our conclusions and told that though the water they supply is not in the hard class this does not mean that softening would not be worth while or preclude them putting forward schemes of doing so if a considerable degree of softening can be effected at a low cost.'

The Water Pollution Research Laboratories[5] have carried out experimental work on the removal of carbonate hardness from a water by æration in the presence of suspended calcium carbonate to furnish nuclei for further precipitation. A typical result showed a reduction from 275 to 150 p.p.m. in about 3 hours, the volume of air used being 8 l. per hour per l. of water.

A tentative specification for 'Cation Exchanger Test Procedures' has been issued by the American Water Works Association.[6] It includes methods of assessment of the physical properties, the exchange values and the chemical composition of cation-exchange materials, as well as some 'research procedures.'

Control of bacterial reproduction in cation-exchange water softeners has been discussed at Chicago.[7] Experimental evidence indicates that both the siliceous and resinous materials are incapable in themselves of supporting bacterial multiplication, but that this may occur on organic matter accumulating in the softener. It is well known that siliceous materials may be effectively disinfected by hypochlorite which is not, however, applicable to all materials. A new sterilizing agent, chloromelamine (trichloro-2 : 4 : 6-triamino-*s*-triazine), was found very suitable for disinfecting both sulphonated phenol–formaldehyde and sulphonated polystyrene resins as well as the siliceous materials.

Disinfection

Two further papers have been published by Ridenour and collaborators on their experimental work comparing the bactericidal effect of chlorine dioxide with that of chlorine. In the first paper[8] the concentrations of the two substances are compared in terms of the *o*-tolidine reaction and on this basis the residuum of chlorine dioxide required (with the water neutral in reaction), is about the same as that of free chlorine. However, the efficacy of chlorine dioxide is increased at a higher p_H, 9·5, whereas that of chlorine is reduced. Hence chlorine dioxide appears very suitable for use with a lime-softened water. As with chlorine, the indicator organism (*Bact. coli*) showed slightly greater resistance than the common water pathogens.

In the second paper[9] the sporicidal properties of chlorine and chlorine dioxide are compared and the results in a pure water show that the latter is more effective. The sporicidal action was also compared in the presence

of some peptone plus 10 p.p.m. of ammonia nitrogen and under these conditions chlorine dioxide was much more effective, because chlorine required very high doses to give a free residual above the breakpoint. It is concluded that 'under conditions where the ammonia content of the water requires breakpoint application of chlorine for control of spores, chlorine dioxide may offer a decidedly superior method of treatment.'

Early in 1949, it was reported[10] that the Metropolitan Water Board have introduced the process of superchlorination at all their filtration works, the process of terminal sterilization by chloramine thus being abandoned. A table was published summarizing bacteriological results in relation to works treating river water with a contact time of only a few minutes for the superchlorination. This table shows a higher percentage of samples negative in 100 ml. with superchlorination than with chloramine treatment. On the basis of the success of superchlorination of the filtered water, it was felt that the expenditure of large quantities of chlorine on prechlorination was no longer justified: The introduction of superchlorination thus resulted in better bacteriological results, and a saving in expenditure on chemicals. The colour of the water has also been improved and complaints of chlorinous taste have ceased. At most of the works, instruments are now in operation for continuous recording of the residual chlorine.

Some experimental results for the rate of destruction of *Bact. coli* by ammonia–chlorine treatment (ammonia followed by chlorine) in well water of high organic quality have been given by Hoather.[11] These results show that the initial rate is very rapid, being comparable with that of free residual chlorine. If the number of bacteria is large, however, a small proportion of them survive this initial phase of rapid action, and are then subject to destruction at a slow rate, comparable with that of residual chloramine. This progressive retardation in rate is doubtless related to the velocity of formation of chloramines and is thus dependent on the temperature of the water and the concentration of the reactants. Increase of temperature is thus not altogether favourable to ammonia–chlorine treatment, and the disadvantage of using too high a dose of ammonia (or of an excess present in the raw water) is explained.

In the control of swimming baths, the policy of maintaining in the water a comparatively high residuum of chlorine such as 1 p.p.m. to 2 p.p.m. is becoming more widespread.[12] The 'breakpoint' action of chlorine is utilized in improving the organic quality of the water and reducing its content of free ammonia to a low figure so that a fairly large proportion of the chlorine is then present as free residual chlorine.

Investigation of the effect of chlorination on the virus of poliomyelitis has been continued in the laboratories of the Michigan Department of Health.[13] A mouse-adapted strain of virus was used, and the preparations were purified by centrifuging to remove practically all associated nitrogenous matter. For the chlorination experiments, 0·25 and 0·5% suspensions of the purified virus were used in three different untreated lake waters, two river waters and one lime-treated well water, some of these waters showing a considerable degree of bacterial impurity. After chlorination the samples were tested for virus content by inoculation into white mice. The doses of chlorine were fairly high (between 1·0 and 4·0

p.p.m. in a large proportion of tests), but the residual concentrations of both free residual chlorine and chloramine were in most instances low. In the untreated surface waters, (p_H approximately 8·0) it was found that the virus was consistently inactivated within 10 minutes in the presence of 0·05 p.p.m. and sometimes by even smaller amounts of free residual chlorine present after this contact period. With the well water at p_H approximately 10 to 11, 0·1 to 0·15 p.p.m. of free residual chlorine was necessary.

The 'Supposed Involvement of Water Supplies in Poliomyelitis Transmission' is discussed by Maxcy[14] who states that:

> 'Although a large number of epidemiological studies of the prevalence and distribution of poliomyelitis have been made during the past half century, there is no instance on record up to the present in which convincing evidence has been presented that pollution of a community water supply was responsible for indirect and widespread exposure of consumers to infection with the virus.'

Analysis with particular reference to residual chlorine

The recommendations of a Joint Committee of representatives of The Institution of Water Engineers, The Royal Institute of Chemistry and The Society of Public Analysts and other Analytical Chemists were published in October as 'Approved Methods for the Physical and Chemical Examination of Water.'[15]

The methods are intended for potable waters and for untreated natural waters such as are commonly purified for public supply purposes. The Committee state that the methods are not necessarily applicable to sewage effluents or to boiler waters which have been dealt with by the Ministry of Health (1929) and the British Standards Institution respectively. They urge that the methods recommended be adopted whenever possible and that any other methods used should only be those giving results in conformity.

The work of the Committee was primarily concerned with the selection of methods of proved reliability, but laboratory experimental work was carried out in relation to certain determinations including that of residual chlorine. Their experiments on the new U.S.A. standard *o*-tolidine method[16] for residual chlorine indicated that it gives rather lower results than the old (1936) standard method. While realizing the shortcomings of the older method which they put forward as standard, they suggest that its use should be continued in this country pending a detailed study of the matter by a new committee comprising representatives of all parties concerned, including the makers of proprietary testing outfits for residual chlorine.

The Committee recommend that all results should be expressed in p.p.m. and a similar recommendation is made in 'British Standard Tests for Water Used in Steam Generation' which was also published in October.[17]

Although a general review of advances in analytical methods for waters will not be given, a paper by Palin[18] on the estimation of free chlorine and chloramine is of particular importance on account of the close relation of such estimations to the control of chlorination. The method presented

is claimed to be the only known procedure capable of giving a clear-cut differentiation between chlorine and chloramines, and also the only practical method available for the quantitative separation of free chlorine, monochloramine, dichloramine and nitrogen trichloride in chlorinated waters. It consists of the addition of the sample to a mixture of hexametaphosphate and neutral *o*-tolidine solution, followed by a series of titrations with standard ferrous ammonium sulphate under conditions which may be summarized as follows :

Titrate until the blue colour is discharged (reading I). Add potassium iodide and mix ; continue titration and note additional volume required (reading 2). Add dilute sulphuric acid, mix and add sodium bicarbonate as specified ; continue titration, noting additional volume required (reading 3). Then reading 1 gives free chlorine (plus two thirds of nitrogen trichloride if present), reading 2 gives monochloramine, and reading 3 gives dichloramine. The distinction between free chlorine and nitrogen trichloride is then made by utilizing the solubility of the latter in carbon tetrachloride. A modified method is given for use in colorimeters.

In commencing a study of 'breakpoint' chlorination using his method, the author finds that nitrogen trichloride is formed with high Cl/N ratios. A note at the end of the paper points out that the process referred to is the subject of a patent application.

Corrosion

The results of an investigation comparing the action of unchlorinated and chlorinated waters on brass ball valves were published early in 1949.[19] The equipment for this work was designed by the Water Pollution Research Laboratory, the valves were selected and examined by the British Non-Ferrous Metals Research Association, and the tests were carried out in five different waterworks where the supply was available for tests before and after chlorination (residuals between 0·1 and 0·4 p.p.m.).

With cast valves made from a single phase α-brass containing 2 to 3% of added lead, it was found that where breakdown of the seating occurred, it was associated with segregation of the lead, and the presence of chlorine had practically no effect on this type of failure.

With the hot-pressed valves also tested there was a tendency to corrosion by dezincification. The presence of chlorine tended to increase the rate of dezincification, but its effect was small compared with that of variation in composition of the water. These results are illustrated by an excellent series of photographs.

Biology

The work of the Freshwater Biological Association[20] has included a continued study of the influence of physical and chemical factors on algal and bacterial counts in the waters of certain lakes. Experiments with *Asterionella* so far indicate that the rate of growth is determined by physical conditions such as illumination and temperature, but that the total population obtained depends on the amount of the essential nutrient which becomes exhausted first. An active increase in numbers of diatoms causes a fall in the concentration of silica in these waters and its cessation can usually be attributed to lack of this element. In connexion with the

chemical analysis of samples of algal cultures an electromagnetically controlled burette capable of delivering amounts of liquid as small as 5×10^{-7} ml. has been developed.

Johnson[21] discusses the distribution of plankton in relation to the thermal stratification of a lake in South California. He discusses the phosphorus and nitrogen cycles and quotes previous work showing that the latter may be assimilated by some plants, including diatoms, from ammonia without nitrification taking place first.

One of the Research Groups of the Institution of Water Engineers[22] is investigating the possibility of the use of ultrasonic radiation in relation to water treatment. For some of the experiments on biological effect, tadpoles have been used and lethal action produced.

Another Group[23] is investigating algal growths, and its main activity so far has been the analysis of information from 60 replies to a questionnaire circulated to the larger British Water Undertakings. It has thus been found that a map of the British Isles may be divided broadly into three zones according to the position of water undertakings experiencing algal troubles :

(1) South-east of a line from Land's End to Spurn Head, the great majority of undertakings using surface supplies experience difficulties every year.

(2) North-west of the line mentioned above, and south of a line drawn from Berwick to the Solway Firth, water undertakings are generally free from serious troubles due to algal growths.

(3) In Scotland, a considerable proportion of the water undertakings experience trouble.

A large majority of algal troubles in treatment plant are connected with slow sand filtration. In this respect pre-filters, micro-straining and prechlorination have all been found useful. Some tables are given for the average of chemical analyses in relation to the occurrence of algal troubles, and for the types of algae involved.

Other aspects of water quality and treatment

Williams[24] experienced trouble due to odour of nitrogen trichloride formed by chlorination above the breakpoint of water derived from a polluted stream. He has adopted the somewhat complex sequence of free residual chlorination, dechlorination, ammoniation and postchlorination to overcome the difficulty.

Besozzi and Baughn[25] describe attempts on a plant scale to treat successfully a lake water having a very high threshold odour value occasionally reaching 7000. Their general conclusion was that treatment of this water on a permanent basis could not be justified, but it is interesting to note that dry fuller's earth was successful in removing a heavy oil film from the raw water, and that chlorinated copperas reduced the content of oil in solution. Free residual chlorine, chlorine dioxide or ozone proved less effective than a very high dose of activated carbon with this water.

Pugh[26] has described the successful use of a nitrifying 'filter' of graded gravel as the first stage in the treatment of a heavily polluted river water,

the rate of 'filtration' being approximately 36 gal. per sq. ft. per hr. He also gives particulars of the Upton-upon-Severn treatment research station of the City of Coventry Water Undertaking, with plant including filters of capacity 2500 gal. per hr.

The effect of mixing different types of water is discussed by Rynarzewski[27] with particular reference to experience at Wroclaw, Poznan and Frankfurt. Some of the sources consist of ferruginous waters, and troubles are experienced due to their admixture either with oxygenated waters, causing some precipitation, or with waters of inferior organic quality resulting in formation of protective colloids.

The influence of seasonal factors on the chemical and bacteriological quality of water from the River Rhine, and of 'bank-filtered' Rhine water from wells supplying the town of Düsseldorf is discussed in detail by Roemer.[28] The content of organic matter is reduced by filtration through the sand, or gravel and organic sediments to one third or one fourth of that in the river water.

A Committee of the American Water Works Association[29] has given official recognition to the procedure of adding fluorine to public water supplies :

> 'In communities where a strong public demand has developed and the procedure has the full approval of the local medical and dental societies, the local and state health authorities, and others responsible for the communal health, the water departments or companies may properly participate in a programme of fluoridation of the public water supplies.'

The present status of fluoridation in the United States has since been reviewed by Faber[30] who discusses the details of the procedure and its anticipated effects. It appears that a total of 17 supplies in nine states are now being treated. Fluorine is, in most instances, applied in the form of sodium fluoride. Smith,[31] however, describes automatic treatment using 60% hydrofluoric acid solution which is available in the U.S.A. in 20-gal. steel drums.

References

1 Sherratt, J. G., *J. Soc. chem. Ind.*, 1949, **68**, 158
2 Henry, C. R., *J. Amer. Wat. Wks. Ass.*, 1949, **41**, 551
3 Langelier, W. F. and Ludwig, H. F., ibid., 163
4 Ministry of Health, "Water Softening" (London : H.M.S.O., 1949)
5 D.S.I.R., "Report of the Water Pollution Research Board with the Report of the Director of Water Pollution Research for the Year 1948" (London : H.M.S.O., 1949)
6 American Water Works Association, *J. Amer. Wat. Wks Ass.*, 1949, **41**, 451
7 Klumb, G. H., ibid., 933
8 Ridenour, G. M. and Armbruster, E. H., ibid., 537
9 Ridenour, G. M., Ingols, R. S. and Armbruster, E. H., *Wat. & Sewage Wks*, 1949, **96**, 279
10 Metropolitan Water Board, 46th Annual Report for the Year ended March 1949 (London : P. S. King & Staples, Ltd., 1949); *Wat. & Wat. Engng.*, 1949, **52**, 134
11 Hoather, R. C., *J. Inst. Wat. Engrs.*, 1949, **3**, 507
12 *Lancet*, 1949, 1056
13 Lensen, S. G., Rhian, M., Stebbins, M. R., Backus, R. C. and Peterson, C. E., *Amer. J. publ. Hlth*, 1949, **39**, 1120
14 Maxcy, K. F., *J. Amer. Wat. Wks Ass.*, 1949, **41**, 696

[15] Institution of Water Engineers, *J. Inst. Wat. Engrs.*, 1949, **3**, 555. (Also reprinted as a separate booklet.)
[16] American Public Health Association and American Water Works Association, "Standard Methods for the examination of Water and Sewage" (New York: 1946).
[17] British Standards Institution, "British Standard Tests for Water used in Steam Generation (Group A: Control Tests for which no laboratory is required)." B.S. 1427: 1949
[18] Palin, A. T., *J. Inst. Wat. Engrs.*, 1949, **3**, 100
[19] Ingleson, H., Sage, A. M. and Wilkinson, R., ibid., 81
[20] Freshwater Biological Association, Seventeenth Annual Report for the Year ending 31st March 1949
[21] Johnson, M. W., *J. Amer. Wat. Wks Ass.*, 1949, **41**, 347
[22] *J. Inst. Wat. Engrs.*, 1949, **3**, 617
[23] Ibid., 329
[24] Williams, D. B., *J. Amer. Wat. Wks Ass.*, 1949, **41**, 441
[25] Besozzi, L. and Vaughn, J. C., ibid., 1035
[26] Pugh, N. J., *J. Inst. Wat. Engrs.*, 1949, **3**, 123
[27] Rynarzewski, Jozef, *Gaz. Woda i Tech. Sanit.* (Poland) 1948, **22**, 308; *J. Amer. Wat. Wks*, 1949, **41**, 50
[28] Roemer, G. B., *Gesundheitsing*, 1948, **69**, 44; *J. Amer. Wat. Wks Ass.*, 1949, **41**, 54
[29] Black, A. P. and Committee, ibid., 575
[30] Faber, H. A., *Wat. & Sewage Wks*, 1949, **96**, 465
[31] Smith, L. A., ibid., 125

SEWAGE, RIVERS POLLUTION AND TRADE WASTES

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THOSE who wish to obtain a bird's-eye view of present-day problems regarding the disposal of sewage, sludge and trade wastes, and the pollution of rivers, could hardly do better than read the able and thoughtful survey of the subject by C. Jepson[1] in his presidential address to the Institute of Sewage Purification. Comments and advice on the management of sewage works and problems connected with them are given with pungency and humour by J. H. Garner.[2] In another paper, J. H. Garner[3] has dealt with legislation on the disposal of sewage and trade wastes, storm water overflows, and the effects of trade wastes on the treatment of sewage, and he regards the standards of the Royal Commission as being satisfactory in general.

F. P. Fischer[4] has speculated on the interesting possibility of carrying out sewage treatment (including sludge digestion) by what he calls the 'Bio-phage nutrient process.' This would involve the use of methods similar in principle to those used in commercial fermentations, namely the use under controlled conditions of pure cultures of specially developed highly active specific organisms; these would have to be grown in special propagation tanks but the plant itself would be more or less conventional though much reduced in size.

Many years ago J. Hurley,[5] in an admirable survey of mechanical flocculation and of the principal factors affecting it, expressed the opinion that the process merited much closer investigation. Now, large-scale experiments on the mechanical flocculation of sewage have been carried out by J. Hurley and W. F. Lester[6,7] who have demonstrated some advantages of the process. The results over a period of seven years at Wolverhampton (Coven Heath Works) have shown that the quality of the tank effluent could be improved by about 20% by the use of mechanical flocculation. This is a notable improvement obtained at little extra cost without using any additional site area.

Under the Public Health (Drainage of Trade Premises) Act 1937, a manufacturer has the right, subject to certain conditions and safeguards, to discharge his wastes into the public sewers for treatment in admixture with sewage at the sewage works. The local authority fixes the terms (e.g. charges, standards for the effluents, etc.) under which such trade effluents may be discharged, but may refuse to admit certain harmful wastes. Those interested in the American approach to problems of handling trade wastes by municipalities should study the Report of the 1945 Committee on Industrial Wastes of the California Sewage Works Association[8] which surveys methods used in handling trade wastes, discusses factors to be considered in arriving at a charge for handling the

wastes, and gives examples of some existing formulæ. G. E. Symons[9] reviews critically special formulæ used by various municipalities in the U.S.A. for calculating the charges to industries for discharging trade wastes to the sewers. The objectionable effects of certain trade wastes on sewage treatment and sludge digestion are discussed by S. E. Coburn,[10] who gives limiting concentrations proposed by the Allegheny County Sanitary Authority for toxic and deleterious wastes received at the sewage treatment plant.

Chlorination of sewage is practised during the summer at the activated-sludge plant at Fort Wayne, Indiana,[11] since the proximity of residences to sports grounds renders some form of odour control necessary. Enough chlorine is used to satisfy about 65–70% of the chlorine demand. The method of automatic control used at the plant is described. A novel method of odour control is reported by G. P. Edwards.[12] Storage of mixed primary and waste activated sludges in tanks in a closed building at the Wards Island, New York sewage treatment plant causes very foul odours which are removed by using a Pease–Anthony scrubber containing Diesel oil to which a small quantity of naphthalene has been added to reduce evaporation. In this way 1 gal. (U.S.) of oil removes the odours from about 200,000 cu. ft. of air; the spent oil can be used as a fuel. Many workers in the U.S.A. (e.g. F. S. Taylor[13] at Oklahoma and J. K. Frei[14] at Springfield) have reported satisfactory results in controlling odours at sewage works by use of 'cloroben' (a mixture of chlorinated benzenes, but mainly *o*-dichlorobenzene). Frei states that treatment of the raw sewage at Springfield with about 1 p.p.m. of cloroben during the summer of 1947, as well as spraying of the channels, screens, grit chambers and grit burial grounds, was effective in controlling odours in the sewage and around the plant. R. Eliassen, A. N. Heller and G. Kisch[15] have developed a new laboratory technique whereby accurate evaluation can be made of the inhibitory action of chlorinated hydrocarbons (e.g. cloroben) on biochemical production of hydrogen sulphide in sewage. Their experiments showed that small doses of cloroben can control formation of hydrogen sulphide from organic sulphur compounds by normal sewage organisms but are not effective for controlling sulphide production from inorganic sulphates. The work indicates the necessity of removing slimes from sewer walls. Some disadvantages of cloroben are its penetrating odour and its toxic effect on sludge digestion. C. W. Beardsley[16] has investigated the nature, growth habits, and methods of control of sewer slimes in the Los Angeles sewer system and considers that slime growths are the chief cause of hydrogen sulphide production in sewage. Thorough cleaning of sewers and treatment with a 10% emulsion of cloroben strongly inhibited slime growths.

The concept of oxidation-reduction potential, E_h (or 'redox' potential) has proved of great value for many years in analytical chemistry and in biochemical studies but it is only comparatively recently that its importance in the interpretation and control of sewage treatment processes has been realized. J. W. Hood,[17] and also J. W. Hood and G. A. Rohlich[18] have described the experimental procedure for determining redox potentials and have given some account of the applications of these measurements for controlling biological processes at a sewage plant. These

applications include the detection of deposits, growths, etc. which might lead to septic conditions in sewers, the detection of toxic substances and industrial wastes, and the determination of conditions inside filters, aeration tanks, and sludge digestion tanks. Positive E_h values are obtained under aerobic conditions, such as should exist in activated sludge plants, sand filters, and low-rate percolating filters working normally. Negative E_h values are obtained under anaerobic conditions, for instance, in sludge digestion and in overloaded high-rate filters. Thus, in activated sludge systems, an E_h value of + 200 to + 600 mv. would be regarded as favourable, but in sludge digestion plants digestion is retarded unless the E_h value is maintained in the region of about − 100 to − 200 mv.

Useful and informative reviews of developments during 1948 in the fields of sewage disposal and treatment, trade waste treatment, and stream pollution have been provided by W. Rudolfs and his collaborators,[19] and by F. W. Mohlman.[20]

Methods of analysis

A comprehensive bibliography (2560 references) of literature on methods of water and sewage analysis published between 1907 and January 1, 1948, has appeared as a special report by the State Engineering Experiment Station, Georgia Institute of Technology.[21] This forms a valuable indexed guide and is arranged in sections each of which deals with an element and its compounds (e.g. nitrogen, sulphur, common and rare metals, etc.) or with a particular property (e.g. acidity, p_H, colour, turbidity).

Notable trends in methods of analysis developed during the past few years are the increasing use of instrumental methods (e.g. use of p_H meters, photoelectric apparatus, etc.) and of organic reagents for the quantitative determination of metals and other constituents.

A good example of the first of these trends is provided by the polarographic method described by E. W. Moore and his associates[22] for the determination of dissolved oxygen in water and sewage. This uses the dropping mercury cathode and may prove useful when continuous recorded observations are required. Another example of the use of instrumental methods is furnished by the somewhat novel procedure suggested by L. R. Setter and his co-workers[23] for the rapid determination of suspended solids in sewage. The sample is homogenized for 30 sec. in a Waring Blendor, the percentage light transmission is determined in a Lumetron Photelometer, and the suspended solids are then estimated from a calibration chart. The curves for raw sewages and final effluents are different. It is claimed that the method enables 10 samples to be tested in 30 min. or less. When the samples are properly homogenized, there is good agreement between results obtained by this method and by the standard Gooch crucible method. Another and more conventional method for determining suspended solids in sewage is described by K. Fraschina,[24] who discusses the many limitations of the standard Gooch crucible method (e.g. excessive time required for filtration, frequency of clogging, dependence of value on asbestos thickness) and gives the precautions needed to obtain accurate results by the use of filter paper. H. F. Ludwig[25] has shown that stirring sewage for 15 min. at a paddle speed of

72 r.p.m. followed by quiescent settlement in an Imhoff cone for 20 min. gives the same removal of 'settleable' solids as does simple settlement over a long period, and based on these observations he suggested a new standard test procedure for determining 'settleable' solids. A spectrophotometric method of determining nitrite in water and sewage by the Griess–Ilosvay method is described by E. P. Baillie[26] who recommends the use of α-naphthylamine hydrochloride instead of the free base. F. B. Strandskov, H. C. Marks and D. H. Horchler[27] have compared the *o*-tolidine method of determining chlorine residuals in chlorinated sewage effluents with a new amperometric method using phenylarsenoxide and they conclude that the new method is the more reliable.

The other trend already referred to, namely the use of organic reagents in analysis, has found expression in a number of interesting papers. M. L. Riehl,[28] and M. L. Riehl and E. G. Will[29] review methods for the determination of metals which affect sewage treatment, and give colorimetric techniques for determining small amounts of iron (potassium thiocyanate), copper (sodium diethyldithiocarbamate, and dithizone), zinc (dithizone), cadmium (dithizone), chromium (diphenylcarbazide), and nickel (dimethylglyoxime). H. G. Swope[30] gives a number of methods for determining metals in industrial wastes. H. G. Swope and her co-workers[31] have made a thorough investigation of the determination of traces of copper in sewage and industrial wastes and recommend a procedure based on digestion of the sample with nitric and sulphuric acids followed by extraction with a carbon tetrachloride solution of dithizone at a p_H of about 2·3.

J. E. Houlihan[32] has described a useful and rapid method for the estimation of ammoniacal nitrogen in sewages and sewage effluents involving addition of 1 ml. of 10% Calgon (sodium hexametaphosphate) followed by direct Nesslerization without distillation. The results are in good agreement with the usual distillation procedure but the method has limitations with tidal-river waters containing high concentrations of salts.

The B.O.D. (biochemical oxygen demand) test continues to attract much attention. W. M. Cameron[33] and V. H. Lewin[34,35] discuss sources of error in the determination of dissolved oxygen and B.O.D., and suggest improved routine methods for the determination of B.O.D. based on the Winkler–azide technique. The effect of sea-water on the biochemical oxidation of sewage has been studied by H. B. Gotaas[36] who found that the oxidation rate constant k is larger for low concentrations of sea-water (up to about 25%) than in fresh water. Increasing concentrations of sea-water cause a decrease in k until in sea-water itself k is less than in fresh water. The carbonaceous or first-stage B.O.D. of sewage is unaffected by sea-water but nitrification is retarded. G. A. Rhame[37] has compared two methods of estimating the total first-stage B.O.D. of sewage. The usual dilution method is used in one method, 3-day and 6-day oxygen demands being determined ; this enables the 5-day B.O.D. as well as the first-stage B.O.D. to be calculated. A chemical method is also described based on oxidation of the sample with potassium dichromate and a mixture of sulphuric and phosphoric acids. With settled sewages there was good agreement between the two methods, but with raw sewage reasonably satisfactory agreement was only obtained by using seeded dilution

water in the dilution method and by straining samples to remove paper. Use of the first-stage B.O.D. as a measure of sewage strength and in the study of polluted streams is advocated. Using a combination of photo-electric cell and recording potentiometer R. S. Ingols[38] has measured the time taken for the decolorization of methylene blue in sewage containing either dissolved oxygen or nitrate nitrogen with the object of developing a short-time B.O.D. test. Unfortunately however the value of the B.O.D. calculated from the decolorization time and the total oxygen available could not be correlated with the dilution B.O.D. value.

The existing tests for free chlorine in water and sewage are subject to many interferences. Hence the publication by R. F. Milton[39] of a new specific test for free chlorine is of some interest. The sample (5 ml.) is treated with a 1% aqueous solution of sodium cyanide (1 ml.) to give cyanogen chloride, then 5 ml. of a 25% aqueous solution of pyridine containing 2% of benzidine hydrochloride are added. A reddish colour develops, reaching a maximum within 10 min., and this can be compared with standards. It is claimed that the test is twice as sensitive as the *o*-tolidine test and is practically specific, only free bromine reacting similarly. The test might have useful applications in sewage analysis though it must be remembered that cyanogen chloride itself would, also respond and it might be formed by chlorination of effluents containing gas liquor.

H. D. Kirschman and R. Pomeroy[40] have described two useful procedures (a wet extraction method, and a method involving flocculation with zinc acetate) for the determination of oil in oilfield waste waters.

Several papers have appeared in America in recent years on the colorimetric determination of phenols in polluted waters by the Gibbs method. In this method 2 : 6-dibromoquinonechloroimide is allowed to react with the very dilute phenol solution at a p_H of about 9·4 to give an indophenol dye. This has a blue, green, or purple colour in the alkaline solution but the colour depends on the nature of the phenol; thus, phenol itself gives a blue-green colour, *o*-cresol a purple colour, *m*-cresol a blue colour and *p*-cresol gives no colour at all. It has now been found that by extraction with organic solvents (e.g. chloroform,[41] *iso*amyl alcohol,[42] *n*-butyl alcohol,[43]) the stability of the colour is increased and the sensitivity multiplied many times. The use of an extraction procedure enables a few parts per billion of phenol to be determined.

Numerous methods have been suggested for the determination of grease in sewage sludges but a somewhat novel one is described by R. J. Stephenson.[44] The sludge is acidified with hydrochloric acid and treated with magnesium sulphate monohydrate. After standing for a few minutes, the mixture solidifies and is removed, ground in a mortar and extracted with light petroleum. A 97% recovery of the grease is thus obtained.

H. Heukelekian and A. J. Kaplovsky[45] give an improved method for determining volatile acids in sewage sludges. Disadvantages of the present method such as presence of sludge solids, changes in concentration of solids, volatile acids and mineral acid during distillation, are obviated by removing sludge by coagulation with acid and ferric chloride followed by vacuum filtration, concentration after making alkaline, and finally

acidification and steam distillation after saturation with magnesium sulphate.

P. Garrick[46] has drawn attention to the serious interference caused by silica in the determination of potash in the ash of composts and sewage sludges. In order to overcome this difficulty it is suggested that the ashed sample should be treated by the Lawrence Smith method (i.e. ignition with ammonium chloride and calcium carbonate).

L. Klein[47,48] has described a semi-micro-Kjeldahl procedure for the determination of nitrogen in sewage sludges, which avoids the use of either a micro-balance or a micro-burette. The method uses only about 100 mg. of sample and results can be obtained in just over an hour.

Sewage

Sewerage and sewage disposal

R. L. Gee[49] discusses methods of sewage disposal at coastal health resorts with special reference to problems at Brighton and Hove (Sussex). Methods of treatment may include screening, settlement, and chlorination but full treatment should rarely be necessary, except possibly during the summer months. There are apparently no standards in Great Britain for the purity of the sea used for bathing, but California requires that the coliform count should not be more than 10 per ml.

H. Lawson[50] has given some account of recent developments in the disposal of sewage at Nottingham. A proposed two-stage sludge digestion plant to deal with sedimentation tank sludge and surplus activated sludge is described. The detention period will be 30 days of which about 20 days will be in the heated primary tanks. The final digested sludge will be used on arable land where it will be conveyed by existing or new sludge-mains.

One of the most valuable papers dealing with plant operation is the account by C. B. Townend and W. T. Lockett[51] of the vast West Middlesex works at Mogden which treats sewage from a population of over 1,200,000 by the diffused air (activated-sludge) process. The authors give a summary and discussion of operating data, plant performance, and analytical results for the eleven-year period from 1936 to 1947. The sewage contains a variety of trade wastes from which a considerable revenue is obtained. Well-nitrified stable effluents are produced averaging 0·83 parts per 100,000 in B.O.D. and 0·7 parts per 100,000 in suspended solids. The mixed raw and surplus activated sludges are digested at 85° F. and the gas produced is used for power while the dried digested sludge is used as a manure.

Sewage disposal in Scotland has made great strides during the past two decades, especially in Lanarkshire, where several small and medium-sized modern activated sludge plants have been constructed.[52,53] These resemble many American plants in their pleasing design and lay-out with their ornamental flower-beds, shrubs, trees, etc. The latest of these plants to be opened is the Clyde Park works of the Burgh of Motherwell and Wishaw (Lanarkshire) where after preliminary screening, grit removal, sedimentation with flocculation by pre-aeration, and grease flotation, biological treatment is given by the diffused air (activated-sludge) process.[54]

Sewage disposal in rural areas is likely to assume greater importance on account of the development of many new water supply schemes and the desirability of protecting our country rivers. The appearance of a paper by E. W. Clark[55] on the design of small sewage works is therefore most opportune. The author regards single-stage biological filtration as the best type of treatment for sewage at a small works. Sludge digestion is not usually economical at a small works. Clinker-filled drying beds are advocated for drying the sludge. J. Harrison[56] has discussed current practice in dealing with the problem of sewage disposal from domestic properties in country districts far away from sewers.

A useful table has been compiled by H. F. Munroe[57] of 36 common chemicals, having applications in water and sewage treatment, with their physical properties, suitable handling materials, characteristics, and main uses.

S. W. Steffensen[58] has described a proposed activated sludge plant for the 26th ward sewage-treatment works, New York, to treat 60,000,000 gal. (U.S.) per day of sewage from a population of 480,000. The effluent will be chlorinated before discharge to Jamaica Bay. Digested sludge will be disposed of at sea or on drying beds.

L. B. Escritt[59] has discussed the design of pipes, valves, and other iron works at sewage works. F. V. Kroeber[60] has suggested protective paints and coatings suitable for aeration tanks, settlement tanks, pipe-lines, sludge digesters, metal parts, and buildings at sewage works.

Martin's well known book on the work of the sanitary engineer has been rewritten and enlarged by L. B. Escritt and S. F. Rich[61] and should be in the hands of every sanitary engineer. Among the subjects dealt with are the sanitation of premises, construction of sewers, siphons, and sea-outfalls, design of sewage disposal works, the activated-sludge process, percolating filters, sludge digestion, and law and administration.

The performance, operation, and design of sewage oxidation ponds in the U.S.A. were discussed some years ago by D. H. Caldwell.[62] These ponds are shallow artificial basins receiving a continuous flow of settled sewage and having a detention period of up to about four weeks. The effluents, which are stable, contain some nitrate and have a low B.O.D., are bacteriologically good compared with effluents from other biological processes. They may, however, be turbid and greenish owing to the presence of algae (especially *Euglena*). Some use has been made of oxidation ponds in California, Nevada, and Arizona, where level land is cheap and easily available, and climatic conditions are favourable (e.g. low rainfall, much sunshine and high air temperatures). The destruction of organic matter is greatest during the long warm summer days when maximum photosynthetic activity occurs. The ponds can also be used to follow conventional biological treatment processes; perhaps the nearest parallel in this country is the clarification lake which receives humus tank effluent at the Esholt works of Bradford Corporation. A committee report has now appeared[63] dealing with the uses and limitations of oxidations ponds in the U.S.A. for the treatment of sewage and trade wastes, and some account is given of their history, development, design, operation and present status. In this report many examples of the use of these ponds for the treatment of trade wastes are quoted. Special reference

is made to trade wastes from seasonal industries (e.g. beet sugar and cannery wastes) but with these it is often desirable to add sodium nitrate to prevent odours.

Activated-sludge process.—Advances made during the past decade in the operation of percolating filters are likely to be paralleled by similar improvements in the activated-sludge process. Much work is being undertaken with a view to improving the Bio-aeration, Simplex, and diffused-air processes. The greatly increased efficiency of the Bio-aeration process obtained by using triangular paddle-blades instead of rectangular ones, and by increasing the speed of rotation was referred to in last year's report. Dome diffusers have been tried at the diffused-air plants at Manchester (Davyhulme) and preliminary results indicate some improvement over the older diffuser plates.

A. Holroyd and H. B. Parker[64] have carried out some fundamental investigations of an exploratory nature on the dynamics of the aeration of water which should be of interest to all concerned with activated-sludge aeration plants.

W. E. Stanley[65] has reviewed operating data of a large number of activated-sludge plants in the U.S.A. A detailed analysis of these data in order to determine factors affecting the efficiency of the process showed that important factors are sewage quantity and quality, chemical character of the sewage, B.O.D. loading, aeration period, solids concentration in mixed liquor, air supply, character and quantity of return sludge, sedimentation efficiency, temperature, and the amount and degree of nitrification. L. S. Kraus[66] gives a mathematical analysis of some of the physical variables requiring control in the activated-sludge process; a high concentration of suspended solids in the aeration tanks is considered to be desirable but this is limited by the pumping facilities available.

Air-diffusion problems at activated-sludge plants are considered by L. R. Setter[67] with particular reference to studies on the clogging of diffuser plates at four of New York's activated-sludge plants. Air-cleaning equipment is essential to prevent internal clogging of the plates. At the Bowery Bay plant, where the atmosphere is relatively dirty, it has been found necessary to clean the air by means of an electrostatic filter. The author also discusses external clogging of plates due to biological growths, fibrous material, sand, and other debris.

D. A. Okun[68] has described unusually interesting laboratory experiments on a modified form of the activated-sludge process, which, if substantiated, might have far-reaching effects on treatment of sewage by activated sludge. Oxygen (used instead of air for aeration) is bubbled through sewage which flows continuously down a tapered aeration tube (maximum oxygen concentration reached is about 35 p.p.m.) and the oxygenated sewage is pumped into the bottom of a long precipitation unit containing suspended biological floc and flows upwards through the floc which is stirred at 9 r.p.m. The effluent is collected in a cone at the top and is used for recirculation. It is claimed that the volume of structure needed to hold the floc is only about 25% of that of conventional aeration tanks and that final sedimentation tanks would be unnecessary.

P. S. S. Dawson and S. H. Jenkins[69] have carried out a painstaking investigation of the oxygen requirements of activated sludge under

various conditions using Warburg and Barcroft respirometers. They found that nearly the whole of the oxygen uptake of the sludge resides in the solid portion and is biological in origin. Important factors affecting oxygen uptake are p_H and temperature. The oxygen uptake is very small below p_H 5 and above p_H 12, the optimum range being p_H 7–8. The sludge is less sensitive to alkaline than to acid conditions. The optimum temperature for oxygen uptake is 28° c. at which temperature oxidation is three times as rapid as at 12° c.

Biological filtration.—Important fundamental work has been carried out by H. Heukelekian[70] on the chemical, biochemical, and biological characteristics of film at different levels of an army camp high-rate filter and a conventional low-rate filter in the U.S.A. He concludes that the nature and mechanism of the purification are the same in both filters and that the differences between them are merely quantitative. Nitrifying organisms occur in both filters but in the high-rate filter the low oxidized nitrogen content of the effluent is due to the short contact period and short period of storage of the film. Protozoa are similar in type in both filters but the high-rate filter has higher numbers of flagellates.

Mainly owing to American work during the past decade, recirculation has now been accepted as an established method of increasing the purifying capacity of a percolating filter. The return of a proportion of effluent to mix with the sewage being treated by the filter may mean that either the filter will treat more sewage and produce as good an effluent or that it will treat the same amount of sewage with production of a better effluent. Different methods of recirculation and theories regarding the increased efficiency of filters when operated under these conditions are discussed by W. Watson and S. R. Twine.[71] One system ('Bio-filtration') whereby filter effluent is returned to the crude sewage for settlement before filtration is considered with special reference to conditions at Keighley, and experiments made to determine the effect of recirculation are described. Studies of the operation of two shallow recirculating filters at Elizabethtown, Kentucky, are reported by W. A. Moore, R. S. Smith and C. C. Ruchhoft.[72] The filters are normally operated in parallel but a better effluent is obtained by series operation. With an average recirculation ratio of 0·63, the best overall filter efficiency with series operation gave an average B.O.D. removal of 88% and the final effluent averaged 24 p.p.m. in B.O.D. H. H. Stanbridge and W. A. Allen,[73] in a survey of possible methods of improving the performance of the Simplex surface aeration plant at Epsom sewage works, suggested that high-rate filtration of the aeration plant effluent with recirculation should do much to improve the effluent. In support of this they describe a small experimental high-rate filter; when dosed with Simplex plant effluent of 990 gal. per cu. yard per day, it converted about 61% of the ammoniacal nitrogen to oxidized nitrogen and gave a final effluent with a daily average 4-hr. oxygen absorption of 0·82. At a small overloaded plant which treated strong domestic sewage from an R.A.F. station by single filtration, improved performance has been reported by E. V. Mills, H. S. Weston, and A. G. Gullan[74] by the use of alternating double filtration; rather better results however were achieved by changing over to recirculation. C. J. Dekema and P. R. Krige[75] describe tests under working

conditions at the Rondebilt (South Africa) Sewage Works comparing two-stage filtration with single-stage filtration in enclosed aerated filters. Two-stage filtration operated in fixed sequence shows at least 30% improvement, and operated with controlled reversal of the filters more than 50% improvement over single-stage filtration.

Removal of fine solids from percolating filter effluents.—Many humus-tank effluents contain suspended matter in excess of the Royal Commission standard (i.e. greater than 3 parts per 100,000); it is in a finely-divided state which is difficult to remove by ordinary methods of settlement. Recently, three comparatively new methods of reducing the suspended solids content of such effluents have been investigated: (i) treatment on pressure filters, (ii) use of micro-strainers, (iii) mechanical flocculation. Experiments on the first two methods are described in an interesting paper by A. E. J. Pettet and his co-workers, with bacteriological investigations by L. A. Allen and his collaborators.[76] It was shown that pressure filters of the backwash type using sand or anthracite as medium could remove finely-divided solids from percolating filter effluents. Semi-scale tests with sand filters gave removals of suspended matter of 67–92% and produced a final effluent having as a rule less than 0·5 parts of suspended solids per 100,000. Similar results were obtained with an anthracite filter. The bacteriological quality of the effluent was also appreciably improved. The use of a micro-strainer (i.e. a rotating drum of woven stainless steel fabric rotating on a horizontal axis) also gave satisfactory results, the reduction of suspended solids being about 70% whilst the final effluents contained only 0·5–1·0 parts of suspended matter per 100,000. Mechanical flocculation of percolating filter effluents using a paddle speed of 15 r.p.m. was tried by J. Hurley and W. F. Lester[6,7] in laboratory experiments on the removal of suspended matter. Satisfactory results were obtained in most cases, the removals of suspended solids being about 50–60% and the suspended solids in the final effluents were only about 1–2 parts per 100,000. Further work is in progress.

No information is yet available on the cost of these three methods. Mechanical flocculation would appear to be the simplest and easiest process to run since it is a continuous process needing but little attention. Pumping would be necessary, as a rule, to work sand filters and they would require periodical cleaning by backwashing. Micro-strainers could be worked by gravity head and they would need washing and intermittent chlorination.

Synthetic detergents and their effect on sewage purification.—The increasing use of synthetic detergents in place of soaps, owing to shortage of fats for soap-making, is causing some concern to sewage undertakings. According to A. L. Waddams,[77] production of synthetic detergents in the United Kingdom has risen from a negligible figure in 1941 to about 10,000 tons in 1948. The character of sewage may, therefore, undergo considerable changes which may entail alterations in operation and possibly increased costs.

W. Rudolfs, R. Manganelli and I. Gellman[78] describe experiments on the effect of a number of American commercial synthetic detergents on various phases of sewage treatment. Although replacement of soaps by detergents may reduce the strenth of sewage (as measured by the

B.O.D. test), settling of solids may be adversely affected and more grease may remain in the tank effluent, thus causing a greater load on the biological treatment to follow. Synthetic detergents can cause much foaming in the activated-sludge process as well as floc agglomeration and carry-over of suspended matter. In concentrations up to 100 p.p.m., synthetic detergents have no appreciable effect on sludge digestion.

Problems arising out of the disposal of effluents containing synthetic detergents are discussed by H. H. Goldthorpe, W. H. Hillier, C. Lumb, and A. S. C. Lawrence.[79] They point out that although only two detergents (Teepol and Lissapol N) are at present widely used in this country, others are on the way, and since each new detergent has slightly different properties, those controlling sewage undertakings are apprehensive about the effects of the discharge of detergents in indiscriminate mixtures in the near future. Reference is also made to adverse effects of detergents on the sedimentation of sewage and on the purification of sewage by activated sludge and by percolating filters. These effects may be especially noticeable in the grease-containing sewages of the West Riding of Yorkshire; here many works at present produce a satisfactory effluent but there is only a small margin of safety, which may be overstepped.

Sewage and public health.—At a conference held in Pretoria in November 1948 several interesting papers were read dealing with public health aspects of sewage and sewage sludge. As A. J. Orenstein has pointed out,[80] the use of sewage effluent and of sewage sludge is vital in a dry country such as S. Africa where every gallon of water and every pound of fertilizer are precious. The possibility of danger to health must be faced, and authorities using sewage products must be prepared to take wisely calculated risks. J. A. McLachlan[81] considers that destruction of ova and cysts of intestinal parasites and of the *Salmonella* group of bacteria in sludge can be achieved if the overall detention time of digestion, drying, and storage is at least three months. H. Wilson[82] deals with the risks of transmission of disease through the use of sewage sludge as fertilizer and gives the warning that organisms responsible for anthrax, bacillary dysentery, typhoid, tuberculosis, amoebic dysentery, hookworm, roundworm, tapeworm, and poliomyelitis can remain viable in *raw* sewage sludge. Methods of eliminating these pathogenic organisms and so rendering sludges safe for use as fertilizers are considered; these include heat treatment, carbonization, chemical processes, and use of aerobic biological agencies (e.g. moulds).

Several workers[83–85] have discussed possible ways, including sewage, in which the virus of poliomyelitis might be spread. Gear and Measrock[85] refer to some important experiments carried out in South Africa which have demonstrated the presence of the virus in raw sludge, settled sewage, septic tank effluent, and humus tank effluent, but not in sewage sludge digested for 30 days, or in a sand filter effluent. Thus, whilst humus tank effluent could contaminate streams with the virus and if used for irrigation might contaminate vegetables or fruit, properly digested sludge on the other hand is free from the virus and safe for use as fertilizer.

Advantages and disadvantages of the chlorination of sewage effluents are discussed by R. Leggat[86] with particular reference to the effects of chlorination on the bacterial content of the effluents and on the prevention

of the spread of disease. When gas liquor is present in sewage, chlorination may increase the toxicity to fish of the final effluent, due to the formation of highly toxic cyanogen chloride,[87] and in such cases chlorination is not advisable. The general feeling at present, however, is against universal chlorination of sewage effluents though it must be admitted that there might be individual cases where chlorination might be desirable.

Biology of sewage purification.—A. N. Barker[88] has discussed the functions of protozoa in sewage purification and the limitations of the use of the method of biological assay of protozoa as a test of pollution.

A short review of the biological aspects of sewage purification, including the functions of protozoa and bacteria in anaerobic and aerobic processes, is given by J. B. Lackey.[89]

In the past, one of the great disadvantages of the percolating filter was the nuisance caused by *Psychoda* and other filter flies ; this difficulty may soon be overcome by the using of the newer synthetic insecticides, DDT and Gammexane. S. H. Jenkins and his co-workers[90] describe experiments on the control of the filter fly *Anisopus fenestralis* by these two insecticides which took place at the Minworth sewage works, Birmingham. Gammexane was found to be cheaper to apply than DDT and it was effective for three to six weeks, only four applications being given between late winter and early summer. T. G. Tomlinson and his associates[91] have carried out experiments on the effect of Gammexane on the control of *Psychoda* and *Anisopus* at a number of heavily loaded sewage works in different parts of England. The flies were successfully controlled with Gammexane dispersible powder at the rate of 16 lb. (about 1 lb. of γ-isomer) per acre in the sewage supplied to the filters. Nearly all samples of effluent from the treated filters tested by bio-assay contained 0·03 p.p.m. or less of Gammexane. Since tests showed that the threshold concentration for the toxicity to trout in tap water was about 0·035 p.p.m., there should be little danger in discharging the effluents to a stream. Experiences in the use of DDT for eradicating *Psychoda* and other flies breeding around the digested sludge drying beds at the Los Angeles sewage plant are given by A. M. Rawn.[92] The treatment (25 lb. of 25% wettable DDT to 150 gallons of water) resulted in the complete disappearance of all flies from the sludge beds. A general review of the use of DDT, Gammexane, and other recently developed synthetic insecticides is given by D. L. Davies.[93]

Sewage sludge

One of the outstanding problems of today in the field of sewage purification is the disposal of sewage sludge. In view of the continued shortage of organic manures, present-day opinion appears to favour the return of sludge to the land. Sewage sludge is of moderate value as a fertilizer but is low in potash and contains only slowly available nitrogen and phosphoric acid, and hence should be supplemented by the use of artificial fertilizers. However, caution should be exercised in using sludge from certain industrial sewages containing toxic metals which may impair its value as fertilizer.

A warning about land disposal of sludge has been given by C. Jepson,[1] who has pointed out that it may not necessarily be the cheapest method

available and that if the use of sludge is necessary to maintain soil fertility, any extra cost in producing the fertilizer should be borne by the nation rather than by the local authority. He puts forward the interesting suggestions that a government committee or a Royal Commission might be appointed to do for sludge disposal what the Iddesleigh Royal Commission did for sewage disposal at the beginning of this century.

In a symposium on sludge disposal, C. Jepson, F. W. Allen, J. P. Todd, N. Cockcroft and L. Klein[94] review some of the methods of disposal used, and discuss the cost, the advantages and the disadvantages of sludge disposal at sea, and disposal by mechanical drying, filter pressing, heat treatment under pressure, land treatment, and vacuum filtration.

A useful series of articles on the pre-conditioning and digestion of sewage sludge, written from the operator's point of view, is given by T. R. Haseltine.[95] Factors involved in the pre-conditioning of the sludge before digestion in lagoons, septic tanks, Imhoff tanks, and separate digestion tanks are given, also methods of measuring the volume of raw sludge before digestion, the concentration of surplus activated sludge, biochemical aspects of sludge digestion, means of controlling acidity, and methods of sludge heating. A warning is given of the injurious effect of certain toxic metals (copper, nickel, mercury, and zinc) on sludge digestion. The author, discussing tests for following the progress of sludge digestion, regards the alkalinity test as the best and suggests an alkalinity of not less than 2000 p.p.m. (as $CaCO_3$) to maintain good active digestion in the first stage of two-stage digestion. H. E. Schlenz,[96] however, prefers to use the determination of volatile acids as a control test; these should lie between 2000 and 3000 p.p.m. (as acetic acid). The volatile-acids test might be especially useful for sludge from industrial wastes high in carbohydrates.

A method of sludge heating which has been widely used in the past is as follows: coils, through which hot water from a boiler circulates, are mounted on the interior walls of sludge digestions. The disadvantage of this method is that sludge cakes on the coils and they are likely to spring leaks, thus making expensive and inconvenient remedial measures necessary. R. A. Greene[97] discusses this and other methods of heating sludge and points out that heating coils are being challenged in the U.S.A. by external heating systems which have the advantages of being more flexible and having more easily accessible parts.

J. H. L. Giles[98] discusses experiences in the use of lime in sludge digesters in Connecticut; he concludes that the liming of heated and unheated digesters and of digestion compartments of Imhoff tanks is beneficial if properly carried out. Lime should be added in small quantities (daily to twice weekly) and mixed with the flow of raw sludge wherever possible. The table on p. 823 is given, serving as a useful guide as to whether digestion is proceeding satisfactorily or not.

It may be noted that the drying times given in this table would not necessarily apply to this country, where climatic conditions are different. In the present writer's opinion, the p_H range for well digested sludge should be somewhat higher than that given, namely 6·6–7·6.

H. G. Leigh[99] describes a scheme being developed at Blackburn (Salmesbury) Sewage Works for digesting sewage sludge, using the digested

sludge as fertilizer for the growing of grass, and using the gas as fuel for drying the grass. It is proposed to sell the dried grass as cattle feed.

The dual disposal of sewage sludge and household refuse by composting to form an organic manure has been successfully carried out at Maidenhead and Leatherhead where they have been producing and selling such composts for many years.[100,101] Some practical aspects of composting have been discussed by C. E. Burke,[102] who is not very enthusiastic about the process, however, and concludes that except for small areas composting cannot be considered as a method of refuse or sludge disposal as normally envisaged. E. H. Sams[103] criticizes some of Burke's conclusions and points out the many benefits to be obtained by composting. For instance at Maidenhead ashes are sold to brickmakers, bottles and metals are collected, and the process of composting works very satisfactorily, the demand for compost exceeding the supply. The distance of the refuse works from the sewage works need be no deterrent since in Holland refuse is sometimes transported for distances as great as 150 miles for conversion into manure.

Characteristics	Well digested sludge	Poorly digested sludge
Colour	Black	Brown or grey
Odour	Tarry	Septic
Appearance	Homogeneous	Individual particles present
Compaction	Excellent	Very poor
Supernatant liquor	Clear	Very turbid
Gasification	Strong	Weak
Drying time	10 days or less	3 weeks or more
pH	6·5–7·0	Less than 6·0
Alkalinity (p.p.m., as $CaCO_3$)	Greater than 1800	Less than 1000

The experiments on the coagulation and vacuum filtration of Manchester sludges, using a semi-scale Dorr–Oliver vacuum filter, described by J. M. Wishart, C. Jepson and L. Klein,[104,105] have now been continued by C. Jepson and G. Greene.[106] Since ferric chloride is now unobtainable in large quantities in this country, their experiments were carried out with chlorinated copperas. Although more chlorinated copperas was required to produce the same result as ferric chloride, and the rate of filtration of the coagulated sludge was slower, chlorinated copperas was nevertheless cheaper to use than ferric chloride. The authors state that by substituting chlorinated copperas for ferric chloride, the cost of producing a ton of dry activated sludge is reduced from £8 6s. 0d. to £7 3s. 0d. and a ton of dry digested sludge from £3 10s. 0d. to £3 3s. 0d. M. A. Groen[107] reports plant-scale tests showing satisfactory results and a saving in costs by using waste steel pickling liquor instead of ferric chloride for conditioning sewage sludge at Dearborn, Michigan.

C. Jepson and L. Klein[108] describe numerous laboratory experiments on the heat treatment of activated sludge and other sewage sludges under various conditions. Heat treatment of sludges at high pressures ('Porteous' process) on the whole gave results similar to those reported by previous workers. However when activated sludge is warmed at ordinary pressures without stirring, the sludge tends to rise to the surface, flotation being nearly complete at about 70° C. This phenomenon, known as 'heat-flotation,' is due to the buoyant effect of minute bubbles of gas; it

appears to have hardly ever been used in the past as a means of densification, but the method has distinct possibilities. The process works equally well with fresh or stale sludges; removals of water are obtained ranging from 50–80%. It is curious that narrow containers give better results than wide containers. The liquors produced were not so strong as those obtained in the 'Porteous' process.

River pollution

The River Boards Act 1948 provides for the formation in England and Wales of some 30 river boards which will replace about 1600 authorities at present dealing with pollution prevention, land drainage, fisheries, etc. The new River Boards, which are now in the process of being set up, will provide an organization based, not on local government areas, but on the natural catchment area so that the river can be considered as a whole. Without effective and up-to-date legal powers, however, these Boards will be greatly hampered in their work. So an important event of the year is the publication of a report[109] by the Ministry of Health dealing with measures for strengthening the law regarding the prevention of pollution of rivers and streams. It is suggested in this report that a number of changes from the Rivers Pollution Prevention Act of 1876 should take place. After a stream survey a River Board should be able to prescribe standards for effluents discharging into rivers; these standards should be prescribed by bye-laws subject to confirmation by the Minister of Health. The standards would not necessarily be uniform but would vary according to the conditions in the stream or part of the stream. Failure to comply with the standards by a manufacturer would mean that the River Board would be able to take proceedings without any consent of the Minister. With regard to tidal waters, full powers for the prevention of pollution should apply only where determined by order of the Minister of Health after a local inquiry; the Minister should not be restricted (as happens at present) merely to 'sanitary grounds' but should be able to take any relevant circumstances into consideration. Further matters dealt with are the control of new openings into streams, solid pollution, innocuous discoloration, and temperature standards for hot effluents. The report adds that all these recommendations should be implemented by a new act repealing the Rivers Pollution Prevention Act 1876; this new act should incorporate existing provisions relating to pollution affecting fisheries (in the Salmon and Freshwater Fisheries Act, 1923). With regard to standards for polluting liquids, the report suggests firstly, that tests would have to be devised to measure some general property of a polluting liquid (e.g. B.O.D., or a toxicity test to fish) and secondly, that standards would be fixed in relation to examination by the standard tests. In fixing these tests, attention would have to be paid to the purposes for which a river water is required. For example, the qualities required in water used for domestic supplies, industry, fishing, agriculture, navigation, or for general amenities would not necessarily be the same. It is recommended that a scientific committee is set up to advise on the tests to be used.

Although conditions in American rivers are quite different from those obtaining in this country, nevertheless in this connexion the observations

of C. C. Agar[110] on standards for trade wastes discharging to rivers in New York State are not without interest. These, as the author emphasizes, represent a minimum standard which is 'dictated by reason, logic, and the requirements of common decency': (i) practically complete removal of settleable and sludge-producing solids, (ii) removal of floating solids, (iii) freedom from visible oil and grease, (iv) no free acid or alkali (p_H range 5·0–9·0), (v) no chemicals in quantities resulting in concentrations toxic to or harmful to man, fish, or aquatic life after admixture with the receiving waters, (vi) reduction of B.O.D. so that the resulting dissolved oxygen in the stream is maintained above 5·0 p.p.m.

American opinion in general, however, appears to favour the use of stream standards rather than effluent standards, and this is understandable in a country having rivers so much larger than those in Great Britain. Several agencies in the U.S.A. concerned with water pollution control in the Ohio River Basin, the Tennessee Valley, West Virginia, and the Potomac River Basin have already put forward water quality standards for boating, bathing, fishing, and water supplies. Those interested in this subject will find a discussion and comparison of these standards in papers by A. H. Stevenson[111] and H. W. Streeter.[112] The standards adopted by the various authorities are not entirely uniform though variations are not great. Particularly interesting are the stream standards proposed for the maintenance of fish life. A daily minimum of 5 p.p.m. of dissolved oxygen is specified for streams in the Ohio River Basin with a monthly average minimum of 6·5 p.p.m., and the corresponding standards proposed by the other authorities are much the same. The recommended p_H ranges are mostly in the region 6·5–8·6.

Following on the publication of three reports on the state of pollution of rivers in England and Wales,[113,114,115] H. D. Turing has now compiled for the British Field Sports Society a fourth report[116] on pollution of Scottish rivers. Although some exaggerations and misleading statements occur in these reports, nevertheless they have done good service in drawing attention to the serious pollution of many of our rivers, to the resulting decline in numbers of salmon and other fish, and to the present unsatisfactory state of the law on pollution. A useful book dealing with the management of rivers in this country, the effects of pollution, fishing, and legislation concerned with the control of rivers has been written by J. W. Kempster.[117] H. W. Streeter[118] has published valuable monographs for the rapid solution of problems of stream sanitation involving the oxygen-sag equation.

V. L. King and his co-workers[119] suggest from data obtained in an investigation of the Raritan River and the Calco Waste Treatment Plant that factories discharging effluents of an acid character to a stream should have the right to use a reasonable and small fraction of the reserve of the river's alkalinity and dissolved oxygen.

M. B. Ettinger and C. C. Ruchhoft[120] have carried out interesting experimental studies on the persistence of phenol and the cresols when added to some inland streams in the U.S.A. Their experiments indicate conclusively that the gradual disappearance of the phenols is due largely to the biochemical action of micro-organisms. Among factors affecting the breakdown of phenols are temperature, characteristics of the flora

and fauna present, microbiological lag, the specific phenolic compound present and its amount, and the presence of nutritional elements (e.g. nitrogen and phosphorus). Breakdown is usually more rapid at 20° C. than at 4° C. Recent pollution by sewage (which provides the necessary nutrients) as well as recent phenolic pollution (which provides phenol-consuming organisms) favour the attack of the phenols but it is difficult to forecast accurately the exact course the removal of phenols will follow.

It seems probable that in the future there will have to be much collaboration between the new river boards now in process of formation, sewage works, industrial undertakings, and waterworks. Water consumption is steadily rising in this country and increasing use is likely to be made of rivers (especially the more polluted reaches) as sources of supply. It is possible that many sewage works and industrial establishments may be called upon to produce effluents of much higher quality than they do now in order to satisfy the requirements of water undertakings. A real difficulty in this is industrial pollution. Thus, in the U.S.A., L. Besozzi and J. C. Vaughn[121] have reported that it has been practically impossible to produce economically a drinkable water free from taste and odours at Whiting, Indiana, on the shores of Lake Michigan as the lake water from which the town draws its supplies is highly polluted by oil refinery wastes.

Trade waste waters

The treatment of trade wastes continues to arouse much interest both in this country and in the U.S.A. The appearance of an excellent book on this subject by B. A. Southgate[122] therefore comes at an opportune time. The book deals comprehensively with the composition, polluting effects, and methods of treatment and disposal of various classes of waste waters, and the effects of pollution on the use of water and on fish are also discussed. An exhaustive list of references to the literature is given. The book is indispensable to all concerned with trade wastes and associated problems of river pollution.

Many important papers on industrial wastes have been published during the year under review. Much of the work is American and noticeable trends in the U.S.A. are the increasing use of biological methods of treatment, especially high-rate anaerobic digestion and high-rate filtration. H. W. Gehm and P. F. Morgan[123] have pointed out that anaerobic digestion may prove to be a most efficient means of obtaining large B.O.D. reductions at relatively low cost with wastes which have a high B.O.D. and which would be costly or difficult to treat by aerobic methods. They list the following as desirable characteristics for wastes to be treated by anaerobic digestion: (i) B.O.D. greater than 500 p.p.m. (ii) C : N ratio at least 1 : 20. (iii) High buffer capacity in relation to organic substances that form volatile acids on decomposition. (iv) Relative freedom from 'settleable' suspended matter. (v) Most of the organic matter should be readily decomposable and of varied type. (vi) Low sulphur content. (vii) p_H around neutral point. (viii) Absence of inhibiting substances. In the discussion on this paper, E. H. Trubnick[124] states that wastes with as low a concentration of solids as 1000 p.p.m. and a B.O.D. as low as 500 p.p.m. can be digested satisfactorily especially

if the solids are mainly dissolved and colloidal. Great stress is laid on the importance of intimate contact between the liquid and the seed sludge which can be secured by intermittent or continuous agitation. Among the wastes which can be treated by anaerobic digestion are distillery wastes,[125] chewing-gum wastes,[126] wool-scouring wastes,[127] yeast wastes,[128] and strawboard wastes.[123]

A novel method of dealing with certain strong soluble non-toxic organic wastes (e.g. penicillin and streptomycin wastes) has been described by H. Heukelekian.[129] It consists in aerating the wastes without flocculent growths by returning the liquid in which the biological growth is dispersed to the raw wastes. Activated sludge cannot be used to treat such wastes because it either disperses or bulks. The seed, which can be developed from soil, consists of finely dispersed cells which normally do not settle. Wastes deficient in nitrogen and phosphorus may require addition of these nutrients. Although the effluents from this process have a higher turbidity than the crude wastes, B.O.D. removals of 70–90% (depending on the strength of the waste) were obtained after 24 hours' aeration. A possible use of the process as a method of pre-treatment before conventional biological methods is indicated.

Wool-scouring wastes.—A simple and comparatively inexpensive method of treating these wastes is described by J. A. McCarthy,[130] and comprises treatment with carbon dioxide (e.g. flue gas) to reduce the p_H to about 8·0, followed by coagulation with calcium chloride (0·8–1·8% of the weight of waste). In some pilot-plant studies, removals of 98% of the suspended solids, 90% of the fats, and more than 70% of the B.O.D. were obtained. It is considered probable that sufficient grease can thus be recovered to cover at least the cost of chemicals and operations. Biological treatment would be necessary for further purification.

S. E. Coburn[131] has compared and discussed most of the methods for dealing with wool-scouring wastes practised in the U.S.A. and gives data on the character of the effluents and sludges produced. Centrifuging removes 25–50% of the fats and is used mainly for producing an effluent which can be re-used in the scouring process. The 'acid cracking' process, involving settlement and subsequent precipitation of fats by adding excess of sulphuric acid has been widely used for many years in the U.S.A. as well as Great Britain. The calcium hypochlorite process[132] is a more recent development consisting essentially of treating the warm settled wastes with calcium hypochlorite, $Ca(OCl)_2$, to reduce the p_H to about 7·5, thus causing separation of much wool grease. The calcium chloride process, already referred to, has only been used so far in pilot-plant tests. The following table[131] compares the relative efficiency of the three main processes for treating wool-scouring wastes :

Treatment process for wool-scouring wastes	Percentage removal of		
	Suspended solids	Fats	5-day B.O.D.
Acid cracking (H_2SO_4)	87·5	77·1	48·6
Calcium hypochlorite	96·2	86·0	42·2
Calcium chloride	99·2	89·6	58·9

The acid cracking process is liable to give objectionable odours, and the effluent is acid. Effluents from all three processes have many times the strength of sewage.

In Yorkshire, wool-scouring wastes are generally disposed of in the sewers and the wool grease is recovered from the sewage. W. H. Hillier[133] has given a fascinating account of the methods adopted for the recovery of grease from the exceptionally strong sewage of Bradford, Yorkshire, and of its processing to give numerous by-products of great commercial value (e.g. rust preventives, lubricants, soaps, waxes, drying oils, and products for blending with oil paints).

Food industry wastes.—In a series of papers W. Rudolfs and E. H. Trubnick[134] have made a detailed study of methods of treating compressed yeast wastes containing highly putrescible organic matter. Chemical methods were ineffective, and biological treatment by activated sludge needed long detention periods and yielded only partial purification. A satisfactory method was found to be a combination of anaerobic digestion and high-rate filtration with recirculation which resulted in B.O.D. reductions of 80–98%.

D. Dickinson[135] describes a recirculating plant for purifying cannery wastes in biological filters and gives results of operation and performance. A bright sparkling effluent was obtained containing some nitrate and having a monthly average B.O.D. of less than 20 p.p.m.

C. N. Sawyer and E. J. Anderson[136] report successful treatment of a mixture of rum wastes and sewage by two-stage biological filtration with recirculation. The reduction in B.O.D. was about 96% and in suspended solids 81–89%. The final effluent contained 1–3 p.p.m. of ammoniacal nitrogen, thus indicating that in the mixture treated enough nitrogen was present to satisfy the nutritional requirements of the aerobic organisms.

The treatment of waste waters from the manufacture of cider has been investigated by E. E. Jones.[137] These wastes are very polluting and have a fairly high B.O.D. (about 1130 p.p.m.) but they have a low nitrogen content. It was shown however that they could be satisfactorily treated in admixture with sewage on percolating filters, but it is emphasized that difficulties might arise if a factory were so placed that domestic sewage was not available for dilution purposes and for supplying sufficient nitrogen.

Metal wastes.—Experiments at the Water Pollution Research Laboratory[138] on the treatment of synthetic steel-pickling wastes have shown that addition of strongly alkaline reagents, such as caustic soda or lime, gave a bulky gelatinous sludge which was very difficult to de-water. On the other hand, conditions favouring the gradual precipitation of the iron sludge produced a fairly granular precipitate of ferric hydroxide which could be easily filtered; these conditions include the use of excess of precipitated chalk, limestone flour, or lime-sludge from a water works, followed by aeration, or else chlorination followed by treatment with limestone flour. H. Kraiker[139] has described profitable processes for converting spent iron pickle liquor (containing 21% of $FeSO_4$ and 0·5% of H_2SO_4) and zinc waste (containing Zn, ZnO, $ZnCl_2$, NH_4Cl, and Fe) into marketable $Fe(OH)_3$, $ZnSO_4$, $ZnCl_2$, and zinc. H. D. Unwin[140] gives

details of a plant for treating alkaline and acid wastes and spent pickle liquor from a ball-bearing factory. Current practice in the disposal of spent steel pickling liquors is surveyed by W. B. Wragge[141] who discusses the construction, operation, maintenance and performance of plants for the treatment of these liquors.

Electroplating wastes are among the most troublesome of metal wastes to deal with, since they may contain such toxic compounds as cyanides, chromates, and salts of copper, cadmium, nickel, and zinc, in addition to acids and alkalis. They can do damage to sewers, where they might be hazardous to workmen, and they can interfere with sewage treatment processes—sludge digestion as well as aerobic processes. A. E. J. Pettet[142] has, therefore, performed a most useful service by reviewing the source and nature of electroplating wastes, their effects on streams and on sewage disposal, and suitable methods of treating them. Of special interest are the methods he has studied for the removal of cyanide. The ferrous sulphate–lime method has the disadvantages of giving an effluent having a residual concentration of about 5 p.p.m. of HCN and of producing a great deal of sludge. The reagents used however are cheap and non-toxic and the final effluent is usually suitable for discharge to the sewers though not to a stream. Another process discussed by Pettet for removing cyanides as well as toxic metals consists of chlorination in alkaline solution (p_H at least 11·0) whereby cyanide is oxidized to cyanate giving an effluent which is innocuous to fish and contains only 0·1 p.p.m. of HCN. Although it has been stated that plants using this process have been operated in the U.S.A.,[143,144,145] little is known about the details and mechanism of the process. In an experimental study of the method the Water Pollution Research Board[138] have now shown that nearly complete destruction of cyanide can be achieved in simple cyanides and in the complex cyanides of copper, zinc, and cadmium, but, as in the case of the ferrous sulphate–lime method, the process does not apply to the more stable nickelocyanides. In experiments with 250-gal. batches,[142] it was noticed that lachrymatory vapours of toxic cyanogen chloride were formed as intermediate product, the reaction apparently occurring in two stages :

$$\mathrm{NaCN + HOCl = CNCl + NaOH}$$
$$\mathrm{CNCl + 2NaOH = NaCNO + NaCl + H_2O.}$$

On the large scale, therefore, treatment would have to be carried out in covered tanks possibly with means provided for extracting the toxic cyanogen chloride vapours. Apparently cyanogen chloride can remain for long periods in the liquid instead of undergoing hydrolysis to cyanate, if the p_H is low enough and insufficient hypochlorite is present.

G. N. Washburn[146] has reported a marked reduction in toxicity to fish (bluegills and brown bullheads) when electroplating wastes are treated in strongly alkaline solution with chlorine. Laboratory studies by G. M. Ridenour[147] have shown that electroplating wastes, after treatment with chlorine in alkaline solution (to remove cyanides and toxic metals) have little effect on the activated sludge process or on sludge digestion unless the ratio of wastes to sewage is abnormally high.

H. Hill[148] has given a useful survey of sewerage in electroplating and related processes used for providing decorative, protective, and wear-resistant surfaces to metals.

It has been reported[149] that electrolysis has been used in the U.S.A. for destroying the cyanides in electroplating wastes; sulphuric acid is added to neutralize any sodium carbonate or cyanate produced.

Radioactive wastes.—The development of nuclear-fission processes since the war has created a new and difficult problem in waste disposal, and work on the safe and convenient disposal of radioactive wastes and of water used for cooling atomic piles is occupying much attention both here and in the U.S.A. J. C. Morris and J. B. Carritt[150] have discussed possible methods of removing radioactive contamination from waters by ion-exchange methods and by coagulation. A. E. Gorman and A. Wolman[151] review in a general way and mainly from the sanitary engineer's point of view the nature of nuclear fission operations as well as problems connected with the disposal of solid, liquid, and gaseous wastes from nuclear fission plants.

The possibilities of disposing of radioactive wastes by biological treatment methods are reviewed in a stimulating paper by C. C. Ruchhoft.[152] When wastes containing minute quantities of radioactive materials are discharged into a river, processes of natural purification reduce the intensity of radioactivity, the reduction being much greater than what could be expected from radioactive decay; this is due to adsorption of the radioactive constituents by the bottom muds and biological flora and fauna. It seems reasonable to assume, therefore, that biological processes might be used to remove radioactivity, and the author discusses the possibility of making use of some modification of the activated sludge process. Experiments at Los Alamos (New Mexico) have shown that, by aeration with activated sludge, more than 95% of plutonium (a long half-life α-emitter) has been removed from sewage containing about 1·4 μg. of plutonium per litre, and transferred to the sludge. The active sludge would have to be dealt with by vacuum-filtration followed by burial of the wet cake in a properly located and protected dumping ground. Many problems and difficulties associated with such a process would be encountered and much further research on various phases of the problem is going on in the U.S.A.

A report on a meeting organized by the U.S. Atomic Energy Commission on the disposal of liquid and gaseous radioactive wastes and on experimental work now in progress is given by A. E. Gorman and W. A. Rodger.[153] Burial is available for highly radioactive wastes with long half-lives. Storage is apparently a suitable method for removing or reducing radioactivity of low intensity due to radio-elements with short half-lives. Thus, at the Oak Ridge National Laboratory (Tennessee), waste cooling water containing mostly short-lived radio-isotopes are passed through underground storage tanks and through a large pond to White Oak Lake, and they eventually reach the Clinch River. Storage in the lake reduces the activity by about 75% and much of the remaining activity is concentrated in the mud and flora at the bottom. The use of ion-exchange resins and chemical precipitation is being investigated. A thick layer of volcanic ash, where available, can be used to absorb

radioactivity due to plutonium. Evaporation of waste waters can be used to separate the radioactivity but this is laborious and expensive.

Miscellaneous wastes.—T. R. Haseltine,[154] in laboratory studies on the treatment of wastes from several proprietary soluble oils, has shown that there were considerable differences in the quantities of coagulant (calcium chloride, aluminium sulphate and lime) required in each case to break the emulsions. Some of the oil wastes responded to treatment by waste pickle-liquor and lime.

Operating data for a pilot plant for treating de-inking wastes by the activated sludge process are given by P. F. Morgan.[155] Primary sedimentation for 1–2 hr. removed 34–40% of the suspended solids and 20–25% of the B.O.D., and 6 hr. aeration with activated sludge removed 68% of the B.O.D. The effluent was still turbid owing to the presence of fine suspended clay. A percolating filter did not give such satisfactory results as activated sludge.

Committee reports on the disposal of wastes from water-softening plants (lime and lime–soda sludges, and brine wastes) have been published in the U.S.A.[156,157] Lime sludges are usually disposed of in beds or lagoons, or into rivers or sewers, but newer methods include use of the sludges as coagulants in sewage treatment, and dewatering followed by calcination to recover lime. Brine wastes from zeolite softening plants may contain chlorides of sodium, calcium, potassium, and magnesium. Methods of disposal include discharge to a stream, storage followed by discharge to stream or sewer, and the use of brine-disposal wells.

A memorandum expressing views on the treatment of gas works effluents has been published.[158] The only feasible method of dealing with spent gas liquors is to discharge them to sewers for treatment at a sewage works; about 0·5% of the volume of the sewage may be accepted but this amount should be reduced if the sewage is an industrial one. Gas tar must be rigidly excluded and the discharge of crude gas liquor should be avoided.

B. W. Dickerson[159] has shown that chemical wastes from the manufacture of synthetic resins, which contain rosin and resin oils, formaldehyde, organic acids, and some domestic sewage, can be treated by high-rate filtration with satisfactory removals of polluting constituents.

C. Lumb, J. P. Barnes and J. Blackburn[160] have described laboratory experiments on the chemical precipitation of Halifax, Yorkshire, sewage which contains a fairly large proportion of greasy and soapy wastes from the textile industries. Chlorinated copperas was found to be superior as a coagulant to sulphuric acid (at present in use on a large scale) but it produced more sludge and was about three times as expensive. The use of chlorinated copperas in conjunction with p_H adjustment with sulphuric acid would be more economical than chlorinated copperas alone.

B. A. Southgate[161] has written a useful review of methods for treating various waste waters from agricultural industries; the wastes dealt with include waste waters produced on farms, dairy wastes, wastes from the canning and drying of vegetables and fruit, slaughter-house wastes, beet sugar wastes, wastes from the manufacture of malt, beer, alcohol, and yeast, and flax-retting wastes. The same author[162,163] has presented a valuable survey of recent advances in methods for treatment of wastes

from paper mills, dairies, canneries, jam factories, viscose rayon manufacture, gas manufacture, pickling of steel and of copper, electroplating, beet sugar manufacture, and flax-retting.

G. Gutzeit[164] has described plant and methods used for the treatment of complex chemical wastes (oily petroleum products, synthetic organic chemicals, acids, etc.) resulting from the cleaning of tank cars used in the U.S.A. to transport various commodities; the cars have often been cleaned with hot caustic soda spray.

References

1 Jepson, C., *Surveyor, Lond.*, 1949, **108**, 375
2 Garner, J. H., ibid., 423
3 Idem, *J. Instn. munic. Engrs.*, 1949, **75**, 784
4 Fischer, F. P., *Wat. & Sewage Wks.*, 1949, **96**, 322
5 Hurley, J., *Surveyor, Lond.*, 1942, **101**, 15
6 Hurley, J. and Lester, W. F., ibid., 1949, **108**, 339
7 Idem, *J. Inst. Sewage Purif.*, 1939, Part 2, 193
8 Report of 1945 Committee on Industrial Wastes of Calif. Sewage Works Assoc., *Sewage Wks. J.*, 1946, **18**, 503
9 Symons, G. E., *Wat. & Sewage Wks.*, 1949, **96**, 200
10 Coburn, S. E., *Sewage Wks. J.*, 1949, **21**, 522
11 Hoot, R. A., *Wat. & Sewage Wks.*, 1949, **96**, 267
12 Edwards, G. P., *Sewage Wks. J.*, 1949, **21**, 795
13 Taylor, F. S., ibid., 1948, **20**, 917
14 Frei, J. K., ibid., 1949, **21**, 158
15 Eliassen, R., Heller, A. N. and Kisch, G., ibid., 457
16 Beardsley, C. W., ibid., 1
17 Hood, J. W., ibid., 1948, **20**, 640
18 Hood, J. W. and Rohlich, G. A., *Wat. & Sewage Wks.*, 1949, **96**, 352
19 Rudolfs, W. *et al.*, *Sewage Wks. J.*, 1949, **21**, 228
20 Mohlman, F. W., *Wat. & Sewage Wks.*, 1949, **96**, 43
21 Weil, B. H., Murray, P. E., Reid, G. W. and Ingols, R. S., Special Report No. 28, State Eng. Expt. Sta., Georgia Institute of Technology, Atlanta, Georgia, U.S.A., 1948
22 Moore, E. W., Morris, J. C. and Okun, D. A., *Sewage Wks. J.*, 1948, **20**, 1041
23 Setter, L.R. *et al.*, ibid., 1949, **21**, 14
24 Fraschina, K., ibid., 221
25 Ludwig, H. F., ibid., 844
26 Baillie, E. P., ibid., 840
27 Strandskov, F. B., Marks, H. C. and Horchler, ibid., 23
28 Riehl, M. L., ibid., 1948, **20**, 629
29 Riehl, M. L. and Will, E. G., 4th Annual Conference on Industrial Wastes, Purdue Univ., Lafayette, Indiana, Sep. 22, 1948
30 Swope, H. G., *Analyt. Chem.*, 1948, **20**, 280
31 Swope, H. G., Hattman, B. and Pellkofer, C., *Sewage Wks. J.*, 1949, **21**, 1016
32 Houlihan, J. E., *Analyst*, 1949, **74**, 511
33 Cameron, W. M., *J. Inst. Sewage Purif.*, 1947, Part 1, 210
34 Lewin, V. H., *Surveyor, Lond.*, 1949, **108**, 281
35 Idem, *J. Inst. Sewage Purif.*, 1949, Part 2, 140
36 Gotaas, H. B., *Sewage Wks. J.*, 1949 **21**, 818
37 Rhame, G. A., *Wat. & Sewage Wks.*, 1949, **96**, 317
38 Ingols, R. S., *Sewage Wks.J.*, 1949, **21**, 984
39 Milton, R. F., *Nature*, 1949, **164**, 448
40 Kirschman, H. D. and Pomeroy, R., *Analyt. Chem.*, 1949, **21**, 793
41 Beshgetoor, A. W., Greene, L. M. and Stenger, V. A., *Ind. Eng. Chem., Anal. Ed.*, 1944, **16**, 694
42 Basavilbaso, F. C., *Rev. Ovras Sanit. Nacion, Buenos Aires*, 1947, **20** (117), 158; *An. Asoc. quim. argent.*, 1947, **35**, 34
43 Ettinger, M. B. and Ruchhoft, C. C., *Analyt. Chem.*, 1948, **20**, 1191
44 Stephenson, R. J., *Analyst*, 1949, **74**, 257

[45] Heukelekian, H. and Kaplovsky, A. J., *Sewage Wks. J.*, 1949, **21**, 974
[46] Garrick, *Nature*, 1947, **60**, 434
[47] Klein, L., *J. Soc. chem. Ind.*, 1947, **66**, 376
[48] Idem, *J. Inst. Sewage Purif.*, 1947, Part 1, 223
[49] Gee, R. L., *J. roy. Sanit. Inst.*, 1949, **69**, 526
[50] Lawson, H., ibid., 706
[51] Townend, C. B. and Lockett, W. T., *J. Inst. Sewage Purif.*, 1947, Part 1, 9
[52] Kirkwood, J. W., ibid., 1943, 176
[53] Ibid., 1947, Part 1, 49, 50, 62
[54] *Surveyor, Lond.*, 1949, **108**, 274
[55] Clark, H. W., ibid., 645, 721, 733
[56] Harrison, J., ibid., 597
[57] Munroe, H. F., *Wat. & Sewage Wks.*, 1949, **96**, 184
[58] Steffensen, S. W., ibid., 205
[59] Escritt, L. B., *Contractors' Rec.*, 1949, **60** (6), 11
[60] Kroeber, F. V., *Sewage Wks. J.*, 1949, **21**, 913
[61] Escritt, L. B. and Rich, S. F., "The Work of the Sanitary Engineer," 1949 (London: Macdonald & Evans)
[62] Caldwell, D. H., *Sewage Wks. J.*, 1946, **18**, 433
[63] Pearse, L. *et al.*, ibid., 1948, **20**, 1025
[64] Holroyd, A. and Parker, H. B. Paper presented at Annual Summer Conference of Institute of Sewage Purification, Harrogate, June 1949; *J. Inst. Sewage Purif.*, 1949, Part 3, 292
[65] Stanley, W. E., *Sewage Wks. J.*, 1949, **21**, 625
[66] Kraus, L. S., ibid., 613
[67] Setter, L. R., *Wat. & Sewage Wks.*, 1948, **95**, 450
[68] Okun, D. A., *Sewage Wks. J.*, 1949, **21**, 763
[69] Dawson, P. S. S. and Jenkins, S. H., ibid., 643
[70] Heukelekian, H., ibid., 1948, **20**, 1032
[71] Watson, W. and Twine, S. R., *J. Inst. Sewage Purif.*, 1949, Part 2, 107
[72] Moore, W. A., Smith, R. S. and Ruchhoft, C. C., *Sewage Wks. J.*, 1949, **21**, 31
[73] Standbridge, H. H. and Allen, W. A., *J. Inst. Sewage Purif.*, 1949, Part 1, 38
[74] Mills, E. V., Weston, H. S. and Gullan, A. G., ibid., 1947, Part, 1, 213
[75] Dekema, C. J. and Krige, P. R., ibid., 1949, Part 1, 91
[76] Pettet, A. E. J. *et al.*, *Surveyor, Lond.*, 1949, **108**, 581, 583, 661
[77] Waddams, *Chem. & Ind.*, **1949**, 783
[78] Rudolfs, W., Manganelli, R. and Gellman, I., *Sewage Wks. J.*, 1949, **21**, 605
[79] Goldthorpe, H. H., Hillier, W. H., Lumb, C. and Lawrence, A. S. C., *Chem. & Ind.*, **1949**, 679
[80] Orenstein, A. J., *J. Inst. Sewage Purif.*, 1949, Part 1, 69
[81] McLachlan, J. A., ibid., 75
[82] Wilson, H., ibid., 78
[83] Maxcy, K. F., *J. Amer. Wat. Wks Ass.*, 1949, **41**, 696
[84] Gear, J. H. S., *J. roy. Sanit. Inst.*, 1949, **69**, 149
[85] Gear, J. H. S. and Measrock, V., *J. Inst. Sewage Purif.*, 1949, Part 1, 82
[86] Leggat, R., *J. roy. Sanit. Inst.*, 1949, **69**, 11
[87] Allen, L. A., Blezard, N. and Wheatland, A. B., *J. Hygiene*, 1948, **46**, 184
[88] Barker, A. N., *J. Inst. Sewage Purif.*, 1949, Part 1, 7
[89] Lackey, J. B., *Sewage Wks. J.*, 1949, **21**, 659
[90] Jenkins, S. H., Baines, S. and Hawkes, H. A., *J. Inst. Sewage Purif.*, 1949, Part 2, 178
[91] Tomlinson, T. G., Grindley, J., Collett, R. and Muirden, M. J., ibid., 127
[92] Rawn, A. M., *Water & Sewage Wks.*, 1949, **96**, 260
[93] Davies, D. L., *J. Inst. Sewage Purif.*, 1949, Part 1, 58
[94] Jepson, C., Allen, F. W., Todd, J. P., Cockcroft, N. and Klein, L., ibid., Part 2, 121
[95] Haseltine, T. R., *Wat. & Sewage Wks.*, 1949, **96**, 143, 195, 271, 355
[96] Schlenz, H. E., *Sewage Wks. J.*, 1944, **16**, 504
[97] Greene, R. A., ibid., 1949, **21**, 968
[98] Giles, J. H. L., ibid., 1072
[99] Leigh, H. G., *J. Inst. Sewage Purif.*, 1949, Part 1, 28
[100] Read, C. T., ibid., 1941, 285

[101] Bould, C., ibid., 1945, Part 2, 79
[102] Burke, C. E., *Surveyor, Lond.*, 1949, **108**, 629, 655, 665
[103] Sams, E. H., ibid., 750
[104] Wishart, J. M., Jepson, C. and Klein, L., Annual Reports, Manchester Rivers Dept., 2 yrs. ending Mar. 31, 1946, Appendix III, p. 37
[105] Idem., *J. Inst. Sewage Purif.*, 1947, Part 1, 140
[106] Jepson, C. and Greene, G., Annual Reports, Manchester Rivers Dept., 2 yrs. ending Mar. 31, 1948, Appendix V, p. 55
[107] Groen, M. A., *Sewage Wks. J.*, 1949, **21**, 1037
[108] Jepson, C. and Klein, L., Annual Reports, Manchester Rivers Dept., 2 yrs. ending Mar 31, 1948, Appendix IV, p. 41
[109] Ministry of Health, Prevention of River Pollution. Report of the Rivers Pollution Prevention Sub-Committee of the Central Advisory Water Committee (H.M.S.O., London, 1949)
[110] Agar, C. C., *Sewage Wks. J.*, 1949, **21**, 1050
[111] Stevenson, A. H., ibid., 110
[112] Streeter, H. W., ibid., 115
[113] Turing, H. D., Pollution, 1. Rivers Trent, Severn, *etc.*, British Field Sports Society, London, June, 1947
[114] Turing, H. D., Pollution, 2. Somersetshire & W. Riding of Yorkshire Rivers, *etc.*, British Field Sports Society, London, Sept., 1947
[115] Turing, H. D., Pollution, 3. Rivers Great Ouse, S. Wales rivers, *etc.*, British Field Sports Society, London, Jan., 1949
[116] Turing, H. D., Pollution, 4. Scottish rivers, *etc.*, British Field Sports Society, London, Feb., 1949
[117] Kempster, J. W., "Our Rivers," 1948 (London: Oxford Univ. Press).
[118] Streeter, H. W., *Sewage Wks. J.*, 1949, **21**, 884
[119] King, V. L. *et al.*, ibid., 534
[120] Ettinger, M. B. and Ruchhoft, C. C., *Ind. Eng. Chem.*, 1949, **41**, 1422
[121] Besozzi, L. and Vaughn, J. C., *J. Amer. Wat. Wks. Ass.*, 1949, **41**, 1035
[122] Southgate, B. A., "Treatment and Disposal of Industrial Waste Waters" (H.M.S.O., London, 1948)
[123] Gehm, H. W. and Morgan, P. F., *Sewage Wks. J.*, 1949, **21**, 851
[124] Trubnick, E. H., ibid., 1949, **21**, 855
[125] Buswell, A. M. and Le Bosquet, M., Junr., *Ind. Eng. Chem.*, 1936, **28**, 795
[126] Logan, R. P. and Rudolfs, W., ibid., 1947, **39**, 1673
[127] Singleton, M. T., *Sewage Wks. J.*, 1949, **21**, 286
[128] Rudolfs, W. and Trubnick, E. H., ibid., 294
[129] Heukelekian, H., *Ind. Eng. Chem.*, 1949, **41**, 1412
[130] McCarthy, J. A., *Sewage Wks. J.*, 1949, **21**, 75
[131] Coburn, S. E., ibid., 84
[132] Faber, H. A., *Sewage Wks. J.*, 1947, **19**, 248
[133] Hillier, W. H., *J. Inst. Sewage Purif.*, 1947, Part 1, 65
[134] Rudolfs, W. and Trubnick, E. H., *Sewage Wks. J.*, 1948, **20**, 1084; 1949, **21**, 100, 294, 491, 700, 1028
[135] Dickinson, D., *J. Inst. Sewage Purif.*, 1949, Part 1, 54
[136] Sawyer, C. N. and Anderson, E. J., *Wat. & Sewage Wks.*, 1949, **96**, 112
[137] Jones, E. E., *J. Inst. Sewage Purif.* 1949, Part 2, 212
[138] D.S.I.R., Report of Water Pollution Research Board with Report of Director of Water Pollution Research for year 1948. (H.M.S.O., London, 1949)
[139] Kraiker, H. Junr., *Chem. Engng.*, 1949, **56**, 112, 144
[140] Unwin, H. D., *Sewage Wks. J.*, 1949, **21**, 501
[141] Wragge, W. B., *J. Iron Steel Inst.*, 1949, **162**, 213
[142] Pettet, A. E. J., Paper read to Electrodepositors' Tech. Soc., Oct. 17, 1949, *J. Electrodepos. Tech. Soc.*, 1950, **25**, 1
[143] Friel, F. S. and Wiest, G. J., *Waterworks & Sewerage*, 1945, **92**, 97
[144] Barnes, G. E., *Wat. & Sewage Wks.*, 1947, **94**, 267
[145] Dobson, J. G., *Sewage Wks. J.*, 1947, **19**, 1007
[146] Washburn, G. N., ibid., 1948, **20**, 1074
[147] Ridenour, G. M., ibid., 1059
[148] Hill, H., *J. Inst. Sewage Purif.*, 1947, Part 1, 167
[149] *Chem. Age, Lond.*, 1949, **60**, 732

[150] Morris, J. C. and Carritt, J. B., *J. New Engl. Wat. Wks. Ass.*, 1948, **62**, 1
[151] Gorman, A. E. and Wolman, A., *Sewage Wks. J.*, 1949, **21**, 63
[152] Ruchhoft, C. C., ibid., 877
[153] Gorman, A. E. and Rodger, W. A., *Chem. Engng.*, 1949, **56**, 116
[154] Haseltine, T. R., *Sewage Wks. J.*, 1949, **21**, 859
[155] Morgan, P. F., ibid., 512
[156] Black, A. P., *J. Amer. Wat. Wks. Ass.*, 1949, **41**, 819
[157] Haney, P. D., ibid., 829
[158] *J. Inst. Sewage Purif.*, 1949, Part 2 ; 104
[159] Dickerson, B. W., *Sewage Wks. J.*, 1949, **21**, 685
[160] Lumb, C., Barnes, J. P. and Blackburn, J., *J. Inst. Sewage Purif.*, 1947, Part 1, 96
[161] Southgate, B. A., "Treatment of Waste Waters from Agricultural Industries," Septième Congrès international des Industries agricoles, Paris, 1948, Q3–A
[162] Southgate, B. A., *Civ. Engng.*, 1948, **43**, 636
[163] Idem., ibid., 1949, **44**, 46
[164] Gutzeit, G., *Sewage Wks. J.*, 1949, **21**, 91

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